QUALITATIVE CHEMICAL ANALYSIS

By the same Author

A TEXT-BOOK OF
QUANTITATIVE INORGANIC ANALYSIS
THEORY AND PRACTICE

A modern treatise for the student, teacher, analytical chemist, and all those concerned with inorganic quantitative analysis.

A TEXT-BOOK OF

QUALITATIVE CHEMICAL ANALYSI

INCLUDING

SEMIMICRO QUALITATIVE ANALYSIS

BY

ARTHUR I. VOGEL, D.Sc. (Lond.), D.I.C., F.I.C.
Head of Chemistry Department, Woolwich Polytechnic:
lately Beit Scientific Research Fellow of the
Imperial College

LONGMANS, GREEN AND CO.
LONDON · NEW YORK · TORONTO

LONGMANS, GREEN AND CO. LTD.
OF PATERNOSTER ROW
43 ALBERT DRIVE, LONDON, S.W.19
NICOL ROAD, BOMBAY
17 CHITTARANJAN AVENUE, CALCUTTA
36A MOUNT ROAD, MADRAS

LONGMANS, GREEN AND CO.
55 FIFTH AVENUE, NEW YORK, 3

LONGMANS, GREEN AND CO.
215 VICTORIA STREET, TORONTO, 1

First published . .	*September 1937*
Second Edition . .	*January 1941*
New Impression . .	*April 1942*
New Impression . .	*November 1942*
Reissue with Appendix .	*September 1943*
New Impression . .	*October 1943*
Third Edition . .	*March 1945*
Reprinted . . .	*April 1946*

PREFACE TO THE THIRD EDITION

THE favourable reception accorded to the second edition of this book by both teachers and reviewers has encouraged the author to think that the general plan—to provide a text-book at moderate cost which can be employed by the student continuously throughout his study of the subject—has continued to meet with approval. In the present edition the text has been submitted to a thorough revision in the light of experience in the laboratory and class-room and of recent advances in qualitative analysis. The chief major additions are :—

(1) A complete Chapter (VIII) devoted to the needs of elementary students and for those whose time for systematic study is limited.

(2) A considerable extension of the systematic tests for acid radicals (or anions).

(3) A Chapter on Semimicro Qualitative Analysis. Particular attention has been devoted to the description of the technique of semimicro analysis, for once this has been mastered, any of the numerous macro procedures described in the book can be readily adapted by the reader to the semimicro scale. The author strongly recommends both teachers and analysts to give semimicro analysis a fair trial and approach the subject with an open mind. The elegance of the tests, the simplicity and low cost of the apparatus, the saving in time and materials, cannot fail to make a strong appeal to all, and it is the writer's firm conviction that in the course of a few years semimicro analysis will largely displace macro analysis in the teaching and practice of qualitative analysis in Great Britain and the British Empire.

The book will be found suitable for students preparing for the Intermediate and Final B.Sc. Examinations of the Universities, for other University Examinations of equivalent standard, and for the Associateship of the Institute of Chemistry ; also for the Preliminary Examination of the Pharmaceutical Society, for the Ordinary and Higher National Certificate in Chemistry, the Higher School Certificate Examinations, the various Scholarship Examinations, as well as for general laboratory use. It is hoped, also, that the volume will be useful to practising analytical chemists.

The author wishes to acknowledge his indebtedness to the

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CHAPTER I

THE THEORETICAL BASIS OF QUALITATIVE ANALYSIS

ELEMENTARY TREATMENT

Qualitative analysis has for its object the identification of the constituents of a substance, of mixtures of substances or of solutions, and the manner in which the component elements or groups of elements are combined with one another. **Quantitative analysis** is concerned with the methods of determining the relative proportions of these constituents. It is evident that rigid qualitative analysis must precede the quantitative analysis; the former should give an approximate indication of the relative proportions of the constituents present and should serve as a guide to the methods to be adopted in the latter.

In what follows, the principles underlying the separation of the more commonly occurring elements will be considered. The treatment will be an elementary one and is designed as an introduction to the subject. By its aid it is hoped that the student will be able to appreciate the significance of the operations commonly employed in qualitative analysis. In addition, a knowledge of the principal reactions of the elements and their derivatives is necessary. Chapters III and IV deal with this aspect of the subject. The ordinary chemical equations are given throughout. The student should have no difficulty, after studying Sects. **I, 24** and **I, 25** in converting most of these into "ionic equations."

The identification of a substance involves its conversion, usually with the aid of another substance of known composition, into a new compound which possesses characteristic properties. This transformation is called a *chemical reaction.* The substance by means of which this transformation is brought about is termed the *reagent.* One distinguishes between reactions in the *wet way* (*i.e.*, those in which a liquid, usually water, is present) and reactions in the *dry way*; the former are by far the more important and will therefore be studied in greater detail.

REACTIONS OF INORGANIC SUBSTANCES IN AQUEOUS SOLUTION

The reactions employed in qualitative analysis are largely the reactions of inorganic acids, bases and salts with each other in aqueous solution. Other solvents are rarely employed except for special operations. It is therefore necessary to have a general knowledge of the conditions that exist in such solutions.

THEORY OF ELECTROLYTIC DISSOCIATION

I, 1. Electrolytes and Non-Electrolytes.—A *solution* is the homogeneous product obtained when a substance is dissolved in water (or any other liquid) ; the dissolved substance is known as the *solute*, and the water (or other liquid) in which the solute is dissolved is called the *solvent*. Substances can be divided into two main classes according to the behaviour of their aqueous solutions to an electric current. In the first class one has those which conduct the electric current and are decomposed thereby ; the second class is composed of those which yield non-conducting solutions. The former are termed *electrolytes*, and these include acids, bases and salts ; the latter are designated *non-electrolytes*, and are exemplified by cane sugar, mannose, glucose, glycerine, ethyl alcohol and urea. It must be pointed out that a substance which is an electrolyte in water, *e.g.*, sodium chloride, may not yield a conducting solution in another solvent such as ether or hexane. Furthermore, electrolytic character is not confined to solutions ; it is also manifested by fused salts.

I, 2. Electrolysis and Ions.—Pure water is a very poor conductor of electricity but, as already stated, when acids, bases or salts are dissolved in it, the resultant solution not only conducts the electric current but is also simultaneously decomposed. The decomposition is called *electrolysis*. Thus, if an electric current from, say, a battery is passed through hydrochloric acid, the hydrogen chloride is split up into hydrogen and chlorine. The hydrogen is liberated at the electrode by which the current leaves the solution (the negative electrode or *cathode*) whilst the chlorine is liberated at the electrode by which the current enters the solution (the positive electrode or *anode*). This behaviour is a general one for electrolytes—for the present it is assumed that no secondary changes occur at the electrodes—and it is obvious that part of the electrolyte moving to the cathode must be positively charged and that moving to the anode must likewise be negatively charged. Faraday termed the charged components of the electrolyte *ions*; the positively and negatively charged ions were called *cations* and *anions* respectively. A diagrammatic figure of electrolysis is shown in Fig. 1.

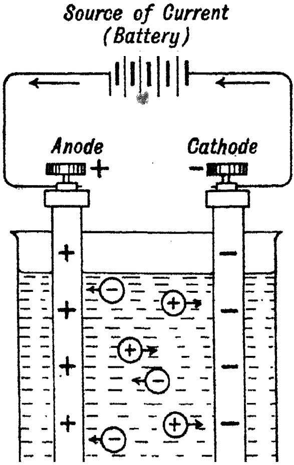

Fig. 1

I, 3. Some Properties of Aqueous Solutions.—It has been found experimentally that equimolecular quantities of non-electrolytes, dissolved in the same weight of solvent, have the same effect upon the lowering of vapour pressure, the depression of freezing point and the elevation of boiling point. The determination of any of these quantities for a solution therefore enables one to calculate the molecular weight of the dissolved substance provided the change produced by one molecular weight in a known weight of solvent is known. Thus the freezing point of water is lowered by 1·86°*C* by the molecular weight of any non-electrolyte dissolved in 1000 grams; the boiling point is similarly raised by 0·51°*C*.

Abnormal results were obtained with electrolytes. Those of the sodium chloride type gave a depression of freezing point of about twice the expected or normal magnitude, whilst with compounds of the type of calcium chloride or sodium sulphate the depression of freezing point was approximately three times that produced by a non-electrolyte of the same molecular concentration.

It was to explain the abnormal vapour pressures, freezing points and boiling points of aqueous solutions of electrolytes that *Arrhenius* in 1887 put forward his *theory of electrolytic dissociation or ionisation.* According to this theory, all electrolytes when dissolved in water are decomposed or dissociated into charged atoms or groups of atoms (ions). The extent of this dissociation or ionisation increases with dilution, and at very great dilutions it is practically complete. For every concentration there is a state of equilibrium between the undissociated molecules and the ions ; the process is a reversible one. The ionisation of compounds may therefore be represented by :

$$NaCl \rightleftharpoons Na^+ + Cl^- ;$$
$$HCl \rightleftharpoons H^+ + Cl^- ;$$
$$CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^- ;$$
$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{--} .$$

The ions carry positive and negative charges and, since the solution is electrically neutral, the total number of positive charges must be equal to the total number of negative charges. The number of charges carried by an ion is equal to the valency of the atom or radical.

The abnormal results referred to above now receive a simple explanation if it be assumed that the effect of each ion upon the vapour pressure, freezing point or boiling point is equivalent to that of a molecule of a non-electrolyte. Sodium chloride yields two ions in aqueous solution, so that the nearly double depression of freezing point obtained in dilute solution would appear to indicate considerable dissociation. The results for sodium sulphate and calcium chloride are similarly accounted for. It is evident that precise measurements of this " abnormality " may be employed to calculate the extent of ionisation or the degree of dissociation. Another method for determining this quantity, dependent upon the measurement of electrical conductivity, will be discussed in a subsequent section.

The phenomena of electrolysis also receive a simple explanation on the basis of the theory of electrolytic dissociation. The conducting power of aqueous solutions of electrolytes is due to the ions which transport the current through the solution. Returning to the example of hydrochloric acid already considered, it is clear that if two inert electrodes, say of platinum, connected to a source of current, be introduced into the solution, the positively charged hydrogen ion H^+ will travel to the cathode from which it will take up one electron, become converted into a neutral hydrogen atom and be discharged. The negatively charged chlorine ion Cl^- will be attracted to the anode; here it will give up its charge, become neutral and be liberated as the free gas. The discharge of the ions is accompanied by a simultaneous dissociation of the electrolyte in order to maintain the equilibrium.

The phenomenon is not always as simple as for hydrochloric acid. The ions are not always discharged at the respective electrodes; they may also react with the electrodes themselves or with the electrolyte or if the potential required to discharge either of the ions be greater than that necessary for the discharge of the ions of water H^+ and OH^- ($H_2O \rightleftharpoons H^+ + OH^-$), either of the latter may be preferentially discharged. Thus in the electrolysis of sodium chloride solution, chlorine is evolved at the anode and the sodium initially formed at the cathode reacts with the water liberating hydrogen; with a mercury cathode, however, the sodium dissolves in the mercury and an amalgam is formed. The electrolysis of a solution of sodium sulphate ($Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{--}$) results in the liberation of hydrogen at the cathode and oxygen at the anode. The latter arises from the circumstance that the sulphate ion SO_4^{--} requires a higher potential for its discharge than does the hydroxyl ion OH^- and hence the latter are discharged in accordance with the equation:

$$4OH^- = 4\epsilon + 2H_2O + O_2.$$

I, 4. Reactions of Ions.—Most of the wet reactions employed in qualitative analysis are reactions of the ions. It is an experimental fact that the compounds of most metals with chlorine (chlorides), which are soluble in water, yield a white precipitate of silver chloride when treated with a solution of silver nitrate. This is because all chlorides give rise to the chloride ion Cl^- in aqueous solution, and this reacts with the silver ion Ag^+ originating from the silver nitrate solution. In a similar manner all silver salts, which dissociate in aqueous solution, will give the same precipitate when chloride ions are added to their solutions. The reactions may be represented:

$$K^+ + Cl^- + Ag^+ + NO_3^- = AgCl + K^+ + NO_3^-;$$
$$Na^+ + Cl^- + Ag^+ + (C_2H_3O_2)^- = AgCl + Na^+ + (C_2H_3O_2)^-;$$
or $$Cl^- + Ag^+ = AgCl.$$

Thus the precipitation of the highly insoluble silver chloride is due to the combination between silver and chloride ions. These ions react independently of the other ions with which they were originally associated in the solid state.

When a solution of potassium chlorate is added to one of silver nitrate, no precipitate of silver chloride is obtained, because potassium chlorate furnishes K^+ ions and ClO_3^- ions in solution but no Cl^- ions. Silver nitrate, dissolved in ethyl alcohol, does not yield a precipitate with chlorobenzene C_6H_5Cl or with carbon tetrachloride CCl_4 in alcoholic solution, although it does so with sodium chloride solution. The sodium chloride is dissociated to a small extent in alcoholic solution; the chlorobenzene and carbon tetrachloride not at all.

I, 5. Dissociation of Acids and Bases in Solution.—An *acid* may be defined as a substance which when dissolved in water undergoes dissociation with the formation of hydrogen ions as the only positive ion:

$$HCl \rightleftharpoons H^+ + Cl^-;$$

$$HNO_3 \rightleftharpoons H^+ + NO_3^-.$$

Actually the free hydrogen ions H^+ (or protons) do not exist in the free state in aqueous solution; they are combined with one molecule of water as the *hydroxonium ion* H_3O^+. The hydroxonium ion is a hydrated proton. The above equations are therefore more accurately expressed by:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-;$$

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-.$$

The dissociation may be attributed to the great tendency of the free hydrogen ions H^+ or protons to combine with water to form hydroxonium ions. Hydrochloric and nitric acids are almost completely dissociated in aqueous solution in accordance with the above equations; this is readily detected by freezing point measurements.

Polybasic acids dissociate in stages. In sulphuric acid, the first hydrogen atom is almost completely ionised:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-,$$

or $$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-.$$

The second hydrogen atom is only partially dissociated, except in very dilute solution :

$$HSO_4^- \quad H^+ + SO_4^{--},$$

or $$HSO_4^- + H_2O \quad H_3O^+ + SO_4^-$$

Phosphoric acid also dissociates in stages :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---};$$

or $$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-,$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{--},$$

$$HPO_4^{--} + H_2O \rightleftharpoons H_3O^+ + PO_4^{---}.$$

The successive stages of dissociation are known as the primary, secondary and tertiary dissociation respectively. As already mentioned, these do not take place to the same degree. The primary dissociation is always greater than the secondary, and the secondary very much greater than the tertiary.

Acids of the type of acetic acid $H.C_2H_3O_2$, give an almost normal freezing point depression in aqueous solution ; the extent of dissociation is accordingly small. It is usual, therefore, to distinguish between acids which are completely or almost completely dissociated in solution and those which are only slightly dissociated. The former are termed *strong acids* (examples : hydrochloric, nitric and iodic acids, primary dissociation of sulphuric acid) and the latter are called *weak acids* (examples : acetic acid, secondary and tertiary ionisation of phosphoric acid, carbonic acid, boric acid and hydrogen sulphide). There is, however, no sharp division between these classes. Methods for the measurement of the relative strengths of acids are described in Section **I, 11.**

A *base* may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydroxyl ions OH^- as the only negative ions*. Thus sodium hydroxide, potassium hydroxide and other metallic hydroxides are almost completely dissociated in aqueous solution :

$$NaOH \rightleftharpoons Na^+ + OH^-;$$

---

* A more general concept of acids and bases is due to Brönsted. He defines an acid as a substance which ionises to yield hydrogen ions or protons, and a base as a substance which combines with hydrogen ions. An acid is therefore a proton donor and a base a proton acceptor. Both can be defined by the expression :

$$A \rightleftharpoons H^+ + B,$$

where A is the acid and B is the base.

these are *strong bases.* Ammonium hydroxide solution, however, is a *weak base.* Only a small concentration of hydroxyl ions is produced in aqueous solution :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \textit{ or } NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$

Salts. The structure of numerous salts in the solid state has been investigated by means of X-rays and by other methods, and it has been shown that ions are actually present in the solid state. Sodium chloride, for instance, is built up of sodium ions and chlorine ions so arranged that each ion is surrounded symmetrically by six ions of the opposite sign ; the crystal lattice is held together by electrostatic forces due to the charges upon the ions. It is not surprising, therefore, that when salts are dissolved in a solvent of high dielectric constant such as water, they are completely dissociated. The complete dissociation of salts in aqueous solution is the modern view and is now almost universally accepted. There are, however, some exceptions, and these have, in some cases, been supported by X-ray measurements. Feebly dissociated salts (weak electrolytes) are exemplified by mercuric chloride, mercuric cyanide, lead acetate and the cadmium halides.

I, 6. Experimental Determination of the Degree of Dissociation —The degree of dissociation of an electrolyte is usually computed either from the freezing point of the solution or from its electrical conductivity. Consider the *freezing point method* first. If one gram molecule of a binary electrolyte is dissolved in 1 litre of water and if a fraction α of the molecule is dissociated, the solution will contain $(1 - \alpha)$ gram molecule of the undissociated electrolyte and 2α gram molecules of ions. The total concentration of the solute will be $(1 - \alpha) + 2\alpha = (1 + \alpha)$ gram molecules. If Δ (*theory*) is the depression of freezing point produced at this concentration by a non-electrolyte (*i.e.*, when no dissociation occurs), Δ (*obs.*) is the observed depression of freezing point, then

$$\Delta\ (obs.)/\Delta\ (theory) = (1 + \alpha)/1 = i \text{ or } \alpha = i - 1.$$

Similarly, if the molecule of the electrolyte gives rise to n ions upon dissociation, the increase in the number of solute particles in the solution will be in the ratio of $1 + (n - 1)\alpha/1$ or

$$\alpha = (i - 1)/(n - 1). \quad \text{Dissociation is complete when } i = n.$$

Some results for sodium chloride and sodium sulphate are tabulated below ; concentrations are expressed in gram molecules per litre. The normal depression for water is 1·86°C (1 gram molecule per 1000 grams).

Sodium Chloride.			*Sodium Sulphate.*		
Concn.	Δ (*obs.*)	a	*Concn.*	Δ (*obs.*)	a
0·0467	0·117°	1·0	0·028	0·141°	0·83
0·117	0·424°	0·93	0·070	0·326°	0·73
0·194	0·687°	0·87	0·117	0·515°	0·68
0·324	1·135°	0·86	0·195	0·817°	0·61

Let us now study the *conductivity method.* The electric current is transferred through the solution by means of the ions, hence the conductance at any temperature, measured in a definite way, will depend upon the degree of ionisation. The *specific resistance* of a solution is the resistance in ohms, measured between parallel faces, of a cube of 1 centimetre side. The reciprocal of the specific resistance is called the *specific conductance* or *conductivity* and is generally represented by the Greek letter kappa (κ). It is measured in " reciprocal ohms " or *mhos* (mho = ohm written backwards). For electrolytic solutions, it is more convenient to employ the *equivalent conductance* or *conductivity* (frequently designated by the Greek symbol lambda Λ) for purposes of comparison. The latter is the conductance of a solution which contains 1 gram equivalent of the solute between two electrodes of indefinite size, 1 centimetre apart. The specific conductance and equivalent conductance are connected by the relation :

$$\Lambda = \kappa V = \kappa/c,$$

where V is the volume in c.c. containing 1 gram equivalent of the solute and c is the concentration in gram equivalents per *cubic centimetre.*

The discovery that the equivalent conductance of aqueous solutions of electrolytes increases with dilution and ultimately reaches a limiting value, was made by Kohlrausch. The Arrhenius theory sought to account for this by assuming that the degree of dissociation increases with increase of dilution until at very great dilutions dissociation is complete. The limiting conductance corresponds to complete dissociation ; it is represented by Λ_0 (when referring to concentrations), or Λ_∞ (when referring to dilutions). The degree of dissociation α, at any concentration c, is given by $\alpha = \Lambda_c/\Lambda_0$, where Λ_c is the equivalent conductance at that concentration. Some results for potassium chloride at 18° are given in Table I.

TABLE I. VARIATION OF EQUIVALENT CONDUCTANCE OF POTASSIUM CHLORIDE WITH CONCENTRATION AT 18°C.

Concentration Gm. equivs./ litre.	*Dilution. V c.c.*	*Specific Conductance.* κ	*Equivalent Conductance.* $\Lambda = \kappa V$	$\alpha = \Lambda_o/\Lambda_o$
0·0001	10,000,000	0·00001291	129·1	0·993
0·01	100,000	0·001220	122·0	0·938
0·02	50,000	0·002395	119·8	0·921
0·1	10,000	0·01120	112·0	0·861
0·5	2,000	0·05100	102·0	0·784
1	1,000	0·09824	98·2	0·757
0		—	130·1	1·000

The variation of equivalent conductance with concentration for a number of electrolytes at 25°C is shown in Table II.

TABLE II. EQUIVALENT CONDUCTANCES AT 25°C.

Concn.	KCl	$NaCl$	HCl	$NaOH$	KOH	$Na.\ C_2H_3O_2$	$H.\ C_2H_3O_2$
0·0001	149·2	125·3					
0·0002	—	—					104·0
0·0005	148·3	124·3	422·2	246·5	270·1	89·4	64·5
0·001	147·5	123·5	421·1	244·7	268·2	88·7	48·7
0·002	146·5	122·2	419·2	242·5	266·2	87·7	35·2
0·005	144·2	119·8	414·9	238·8	262·1	85·7	22·8
0·01	141·6	117·8	410·5	234·5	258·9	83·7	16·2
0	150·1	126·2	423·7	260·9	283·9	91·3	388·6

For strong electrolytes, the limiting conductance Λ_0 may be determined by extending the measurements to low concentrations and then extrapolating the conductivity-concentration curve to zero concentration. For weak electrolytes, such as acetic acid and ammonium hydroxide, this method cannot be employed since the dissociation is nowhere near complete at the lowest concentrations at which measurements can be conveniently made (*ca.* 0·0001N). Another method is, however, available for estimating Λ_0. This is described in the following section.

I, 7. The Independent Migration of Ions.—As a result of a prolonged and careful study of the conductance of salt solutions down to low concentrations, Kohlrausch found that the equivalent conductance of an electrolyte is made up of the sum of the limiting equivalent conductances of the component ions. This permits one to predict Λ_0 by adding together numbers which are characteristic of the ions in the solution. The relation is :

$$\Lambda_0 = \lambda_{0c} + \lambda_{0a},$$

where λ_{0a} and λ_{0c} are the limiting conductances or *mobilities* of the anion and cation respectively. The ionic mobilities are computed from Λ_0 with the aid of *transport numbers*; these represent the fraction of the current carried by the cation and anion respectively, and are obviously proportional to their respective speeds. (For a fuller discussion of transport numbers, the student is referred to text-books of physical chemistry.) Thus for potassium chloride at 18°, $\Lambda_0 = 130{\cdot}1$, n_a the anion transport number is 0·503 (after Kohlrausch and Maltby), hence

$$\lambda_{0a} = \lambda_{Cl^-} = 0{\cdot}503 \times 130{\cdot}1 = 65{\cdot}5,$$

and $$\lambda_{0c} = \lambda_{Na^+} = 0{\cdot}497 \times 130{\cdot}1 = 64{\cdot}6.$$

When one pair of mobilities is known, others may be computed from the relation, also discovered by Kohlrausch, that the difference between the values of Λ_0 for two anions is independent of the cation and *vice versa*. In this manner, a table of mobilities can be constructed. Some limiting ionic mobilities at 18°*C* and 25°*C* are collected in Table III. This may be utilised for the determination of the limiting conductance of any electrolyte. Its particular value is for weak electrolytes where Λ_0 cannot be determined by direct extrapolation. Thus for acetic acid at 25°,

TABLE III. LIMITING IONIC MOBILITIES AT 18°*C* AND 25°*C*

18°*C*				25°*C*			
H^+	317·0	OH^-	174·0	H^+	348·0	OH^-	210·8
Na^+	43·5	Cl^-	65·5	Na^+	49·8	Cl^-	76·4
K^+	64·6	NO_3^-	61·8	K^+	73·4	IO_3^-	42·0
Ag^+	54·4	Br^-	67·7	Ag^+	61·9	$C_2H_3O_2^-$	40·6
$1/2\ Ca^{++}$	52·2	I^-	66·1				
$1/2\ Sr^{++}$	51·7	F^-	46·8				
$1/2\ Ba^{++}$	55·0	ClO_3^-	55·0				
$1/2\ Pb^{++}$	61·6	IO_3^-	34·0				
$1/2\ Cd^{++}$	46·5	$C_2H_3O_2^-$	32·5				
$1/2\ Zn^{++}$	46·0	$1/2\ SO_4^{--}$	68·3				
$1/2\ Cu^{++}$	45·9	$1/2\ C_2O_4^{--}$	61·1				

$$\Lambda_0 = \lambda_{C_2H_3O_2^-} + \lambda_{H^+} = 348{\cdot}0 + 40{\cdot}6 = 388{\cdot}6.$$

The degree of dissociation at any concentration can then be calculated from the relation $\alpha = \Lambda_c/\Lambda_0$, where Λ_c is the equivalent conductance at that concentration. A few typical results, calculated in this manner, are collected in Table IV.

TABLE IV. DISSOCIATION OF ACIDS AT 25°C

	Degree of Dissociation.	
	0·5N	0·001N
Strong Acids.		
Hydrochloric acid	0·862	0·993
Sulphuric acid (primary ionisation) ...	0·536	0·960
Nitric acid	0·862	0·997
Trichloroacetic acid	0·760	0·994
Weak acids.		
Acetic acid	0·006	0·126
Carbonic acid	0·0008	0·017
Hydrocyanic acid	0·00005	0·0011

It is evident that the degree of dissociation varies considerably both with the nature of the acid and with the concentration. The *strengths* of acids can be *roughly* compared in terms of α at any given concentration. This method of comparison divides the acids into two main groups: *strong acids*, which are largely dissociated, and *weak acids*, which are feebly dissociated in aqueous solution. Considerable variations occur amongst the weak acids, and more accurate methods for the comparison of their strengths will be discussed under the law of mass action (Section **I, 9**).

I, 8. Theory of Complete Dissociation. Interionic Attraction Theory of Debye, Hückel and Onsager.—It has already been pointed out that strong electrolytes, particularly salts and bases, are completely dissociated in aqueous solution. How then is one to explain the increasing equivalent conductance with decreasing concentration? We have seen that Arrhenius ascribed this to the increasing degree of dissociation, the mobilities of the ions at all concentrations being assumed constant. This classical view can now no longer be held to possess any significance for strong electrolytes. Debye and Hückel in 1923 and Onsager in 1925 accepted the complete dissociation theory, and attributed the changes in conductance with dilution (and also the associated changes in osmotic activity in dilute solutions) to the electrical forces between the ions. Owing to the interionic forces, each ion will build up an "atmosphere" of ions of opposite sign. When an electromotive force is applied, the ionic "atmosphere" will be unsymmetrical, for the ion has to build up a new ionic "atmosphere" in front, whilst the "atmosphere" behind the moving ion will be dispersed. The dispersal of the ionic "atmosphere," however, requires a certain amount of time ("time of relaxation"), and hence there will always be, in the rear of the moving ion, an excess of ions of opposite sign as a result of which the mobility will be diminished. Further, the motion of, say, a positively charged reference ion will be subject to a retardation by the movement of the negative ions in the opposite direction, and the effect will be that of a viscous electrical drag ("electrophoretic effect"). In short, the speed of the ions will be diminished because of the attractive forces exerted by the ions constituting the "atmosphere" of opposite sign. The attractive forces will clearly be greater the more concentrated the solution, since the ions are brought closer together. Consequently the mobility of the ions will decrease with increasing concentration. At extreme dilutions the interionic forces will become negligibly small owing to the relatively great distance between the ions, and the mobilities will approach a maximum value. The change in equivalent conductivity is thus attributed, not as in the Arrhenius theory to changes in the degrees of dissociation or to changes of the number of ions, but to variations in the velocities of the ions due to interionic forces. Debye, Hückel and Onsager have deduced an expression which accounts satisfactorily for the variation of the equivalent conductance with concentration of strong electrolytes from the lowest concentration to about $0{\cdot}002N$: it may be expressed in the form that Λ_c is proportional to the square root of the concentration. At higher concentrations deviations occur, and many, at present, empirical assumptions are introduced to express the relationship between Λ_c and the concentration over a larger concentration range. The deviations may be regarded as due to some form of ionic association, such as the formation of ionic doublets which may behave, in some respects, as unionised molecules. The extent to which this occurs will depend upon the interionic forces and upon the chemical nature of the ions of the solvent, since many ions possess a tendency to undergo solvation, *i.e.*, to combine with the molecules of the solvent.

It is important to realise that whilst complete dissociation occurs with strong electrolytes, this does not mean that the *effective concentrations* of the ions are the same at all concentrations, for if this were the case, the osmotic properties of aqueous solutions could not be accounted for. The variation of osmotic properties is ascribed to changes of the *"activity"* of the ions; these are dependent upon the electrical forces between the ions. Expressions for the variations of the activity or of related quantities, applicable to dilute solutions, have also been deduced from the Debye-Hückel-Onsager theory. Further consideration of the conception of " activity " will be given in the following section.

I,9. THE LAW OF MASS ACTION.

Guldberg and Waage in 1867 clearly stated the law of mass action in the form: the velocity of a chemical reaction at constant temperature is proportional to the product of the concentrations of the reacting substances. The concentrations are usually expressed in gram molecules per litre. On applying the law to homogeneous systems, *i.e.*, to systems in which all the reacting molecules are present in one phase, for example in solution, one can arrive at a mathematical expression for the conditions of equilibrium in a *reversible reaction.*

Consider first the simple reversible reaction at constant temperature:

$$A + B \rightleftharpoons C + D.$$

The velocity with which A and B react is proportional to their concentrations, or

$$v_1 = k_1 \times [\mathbf{A}] \times [\mathbf{B}],$$

where k_1 is a constant known as the *velocity coefficient*, and the square brackets in heavy type indicate the molecular concentrations of the substance enclosed within the brackets. Similarly, the velocity with which the reverse reaction occurs is given by

$$v_2 = k_2 \times [\mathbf{C}] \times [\mathbf{D}].$$

At equilibrium, the velocities of the reverse and forward reactions will be equal (the equilibrium is a dynamic and not a static one) and therefore $v_1 = v_2$,

or $$k_1 \times [\mathbf{A}] \times [\mathbf{B}] = k_2 \times [\mathbf{C}] \times [\mathbf{D}],$$

or $$\frac{[\mathbf{C}] \times [\mathbf{D}]}{[\mathbf{A}] \times [\mathbf{B}]} = \frac{k_1}{k_2} = K.$$

K is the *equilibrium constant*; it will vary somewhat with the temperature and pressure, but such variations are of relatively little importance in qualitative analysis.

The expression may be generalised. For a reversible reaction represented by:

$$p_1A_1 + p_2A_2 + p_3A_3 \rightleftharpoons q_1B_1 + q_2B_2 + q_3B_3,$$

where p_1, p_2, p_3 and q_1, q_2, q_3 are the number of molecules of the reacting substances, the condition for equilibrium is given by the expression:

$$\frac{[B_1]^{q_1} \times [B_2]^{q_2} \times [B_3]^{q_3}}{[A_1]^{p_1} \times [A_2]^{p_2} \times [A_3]^{p}} = K.$$

Expressing this in words, it may be stated: When equilibrium is reached in a reversible reaction, at constant temperature, the product of the molecular concentrations of the resultants (the substances on the right-hand side of the equation), divided by the product of the molecular concentrations of the reactants (the substances on the left-hand side of the equation), each concentration being raised to a power equal to the number of molecules of that substance taking part in the reaction, is constant.

I, 10. Application of the Law of Mass Action to Solutions of Electrolytes.—Attention has already been directed to the fact that weak electrolytes, such as acetic acid and ammonium hydroxide, undergo reversible dissociation when dissolved in water. The equilibrium between the undissociated molecules and the ions for such electrolytes can be investigated by means of the law of mass action. The law cannot be applied to strong electrolytes, such as salts, where dissociation is complete, since there is little or no equilibrium between the ions and the undissociated molecules in solution.

The equilibrium which exists in a dilute solution of acetic acid is:

$$H.C_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-.*$$

Applying the law of mass action, we have:

$$[C_2H_3O_2^-] \times [H^+] / [H.C_2H_3O_2] = K.$$

K is the *ionisation constant* or *dissociation constant* at constant temperature. The term *affinity constant* is sometimes employed for acids and bases. If one gram equivalent of the

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* Strictly speaking the equilibrium should be written:

$$H.C_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-;$$

the older form will, however, be retained for the sake of simplicity.

electrolyte is dissolved in V litres of solution ($V = 1/c$, where c is the concentration in gram equivalents per litre), and if α is the degree of dissociation at equilibrium, then the amount of undissociated electrolyte will be $(1-\alpha)$ gram equivalents, and the amount of each of the ions will be α gram equivalents. The concentration (gram equivalents per litre) of undissociated acetic acid will therefore be $(1-\alpha)/V$, and the concentrations of each of the ions α/V. Substituting in the equilibrium equation, one obtains the expression :

$$\alpha^2/(1-\alpha)V = K \qquad \{\text{or } \alpha^2c/(1-\alpha) = K\}.$$

This is known as "*Ostwald's dilution law.*" The agreement of the "law" with experiment is illustrated by the following results for acetic acid at 25°C (Table V).

TABLE V. EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C.

Concn. × 10^4	Λ_c	α	$K \times 10^5$
1·873	102·5	0·264	1·78
5·160	65·95	0·170	1·76
9·400	50·60	0·130	1·83
24·78	31·94	0·080	1·82
38·86	25·78	0·066	1·83
56·74	21·48	0·055	1·84
68·71	19·58	0·050	1·84
92·16	16·99	0·044	1·84
112·2	15·41	0·040	1·84
0	388·6		

The mean classical or Ostwald dissociation constant of acetic acid at 25° is $1{\cdot}82 \times 10^{-5}$. Similar results—the individual variations may sometimes be slightly greater—are obtained for other weak electrolytes.

I, 11. Strength of Acids and Bases.—It has already been stated that the properties of acids are the properties of the hydrogen ion H^+ (or, more correctly, the hydroxonium ion H_3O^+). For any given total concentration of acid, the concentration of the hydrogen ions will depend upon the degree of dissociation α; the strength of an acid will thus depend upon the value of α at a given concentration. The dissociation constant gives a relationship between α and the concentration, and it accordingly also represents a measure of the strength of the acid or a measure of its tendency to undergo dissociation.

The properties of bases, according to the most elementary view, depend upon the hydroxyl ion* and the ionisation constant will likewise be a measure of the strength of the base.

For very weak or slightly dissociated electrolytes, the expression $\alpha^2/(1-\alpha)V = K$ reduces to $\alpha^2 = KV$ or $\alpha = \sqrt{KV}$, since α may be neglected in comparison with unity. Hence for any two weak acids or bases at any given dilution V (in litres), one has $\alpha_1 = \sqrt{K_1V}$ and $\alpha_2 = \sqrt{K_2V}$, or $\alpha_1/\alpha_2 = \sqrt{K_1}/\sqrt{K_2}$. Expressed in words, for any two weak or slightly dissociated electrolytes at equal dilutions, the degrees of dissociation are proportional to the square roots of their dissociation constants. Some values for the dissociation constants at 25° for weak acids and bases are collected in Table VI.

TABLE VI. DISSOCIATION CONSTANTS AT 25°*C*.

	Monobasic Acids.		
Nitrous acid	$4{\cdot}6 \times 10^{-4}$	Cyanoacetic acid	$3{\cdot}49 \times 10^{-3}$†
Hydrocyanic acid	$7{\cdot}2 \times 10^{-10}$	Phenylacetic acid	$4{\cdot}88 \times 10^{-5}$†
Formic acid	$1{\cdot}77 \times 10^{-4}$†	Benzoic acid	$6{\cdot}37 \times 10^{-5}$†
Acetic acid	$1{\cdot}82 \times 10^{-5}$	*o*-Chlorobenzoic acid	$1{\cdot}20 \times 10^{-3}$†
	$1{\cdot}76 \times 10^{-5}$†	*o*-Nitrobenzoic acid	$6{\cdot}00 \times 10^{-4}$†
	Dibasic Acids.		
Hydrogen sulphide	K_1 $9{\cdot}1 \times 10^{-8}$ K_2 $1{\cdot}2 \times 10^{-15}$	Oxalic acid	K_1 $5{\cdot}9 \times 10^{-2}$† K_2 $6{\cdot}4 \times 10^{-5}$†
Sulphurous acid	K_1 $1{\cdot}7 \times 10^{-2}$ K_2 $1{\cdot}0 \times 10^{-7}$	Malonic acid	K_1 $1{\cdot}40 \times 10^{-3}$† K_2 $2{\cdot}20 \times 10^{-6}$†
Sulphuric acid	K_2 $1{\cdot}15 \times 10^{-2}$†	Succinic acid	K_1 $6{\cdot}63 \times 10^{-5}$† K_2 $2{\cdot}54 \times 10^{-6}$†
Carbonic acid	K_1 $4{\cdot}31 \times 10^{-7}$† K_2 $5{\cdot}61 \times 10^{-11}$†	*d*-Tartaric acid	K_1 $1{\cdot}04 \times 10^{-3}$† K_2 $4{\cdot}55 \times 10^{-5}$†
	Tribasic Acids.		
Phosphoric acid	K_1 $7{\cdot}52 \times 10^{-3}$† K_2 $6{\cdot}23 \times 10^{-8}$† K_3 5×10^{-13}†	Citric acid	K_1 $9{\cdot}20 \times 10^{-4}$† K_2 $2{\cdot}69 \times 10^{-5}$† K_3 $1{\cdot}34 \times 10^{-6}$†
	Bases.		
Ammonium hydroxide	$1{\cdot}8 \times 10^{-5}$ $1{\cdot}79 \times 10^{-5}$†	Aniline	$4{\cdot}0 \times 10^{-10}$
Methylamine	$4{\cdot}38 \times 10^{-4}$†	Pyridine	$2{\cdot}0 \times 10^{-9}$
Dimethylamine	$5{\cdot}20 \times 10^{-5}$†	Quinoline	$6{\cdot}0 \times 10^{-10}$
Trimethylamine	$5{\cdot}45 \times 10^{-5}$†	Piperidine	$1{\cdot}3 \times 10^{-3}$

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* See footnote, Section **I, 5.**

† Figures marked with a † are the true or thermodynamic dissociation constants (see Section **I, 12**).

I, 12. Activity and Activity Coefficient.—In our deduction of the law of mass action, it was assumed that the effective concentrations or active masses of the components could be expressed by the stoichiometric concentrations. According to modern thermodynamics, this is not strictly true. The rigid equilibrium equation for, say, a binary electrolyte:

$$AB \rightleftharpoons A^+ + B^-,$$

is

$$a_{A^+} \times a_{B^-} \,/\, a_{AB} = K_a,$$

where a_{A^+}, a_{B^-} and a_{AB} represent the *activities* of A^+, B^- and AB respectively, and K_a is the *true* or *thermodynamic dissociation constant.* The concept of *activity,* a thermodynamic quantity, is due to G. N. Lewis. This quantity is related to the concentration by a factor, termed the *activity coefficient*:

activity = concentration × activity coefficient.

Thus at any molar concentration

$$a_{A^+} = f_{A^+}.[A^+],\ a_{B^-} = f_{B^-}.[B^-]$$

and $a_{AB} = f_{AB}.[AB]$, where f refers to the activity coefficients, and the square brackets to the molar concentrations. Substituting in the above equation, one obtains:

$$\frac{f_{A^+}.[A^+] \times f_{B^-}.[B^-]}{f_{AB}.[AB]} = \frac{[A^+].[B^-]}{[AB]} \times \frac{f_{A^+} \times f_{B^-}}{f_{AB}} = K_a.$$

This is the rigorously correct expression for the law of mass action as applied to weak electrolytes.

The activity coefficient varies with the concentration. For ions, it varies with the valency, and is the same for all dilute solutions having the same *ionic strength,* the latter being a measure of the electrical field existing in the solution. The term *ionic strength,* designated by the symbol μ, was introduced by Lewis and Randall in 1921, and is defined as equal to one half of the sum of the products of the concentration of each ion multiplied by the square of its valency, or $\mu = \frac{1}{2}\Sigma c_i z_i^2$, where c_i is the ionic concentration in gram mols per litre of solution. An example will make this clear. The ionic strength of 0·1 molar HNO_3 solution containing 0·2 molar $Ba(NO_3)_2$ is given by:

$$1/2\ \{0{\cdot}1 \text{ (for } H^+) + 0{\cdot}1 \text{ (for } NO_3^-) + 0{\cdot}2 \times 2^2 \text{ (for } Ba^{++}) + 0{\cdot}2 \times 2 \text{ (for } NO_3^-)\}$$

$$= 1/2\ \{1{\cdot}4\} = 0{\cdot}7.$$

The activity coefficient depends upon the *total* ionic strength of the solution in a manner which cannot be discussed in this book. Generally speaking, it is comparatively difficult to determine activity coefficients experimentally, particularly in concentrated solutions and in mixtures of ions of several valency types. The activity coefficient of unionised molecules does not differ considerably from unity. For weak electrolytes in which the ionic concentration and therefore the ionic strength is small, the error introduced by neglecting the difference between the actual values of the activity coefficients of the ions, f_{A^+} and f_{B^-}, and unity is small ($< 5\%$). Hence for weak electrolytes, the true or thermodynamic expression reduces to $[A^+] \times [B^-] / [AB] = K$; the constants obtained by the use of simple concentrations will be accurate to 2–6%. Such values are sufficiently precise for purposes of calculation in qualitative analysis. It must, however, be pointed out that precision values for the dissociation constants of weak electrolytes can be obtained by the use of special methods; the discussion of these is outside the scope of this volume.

Strong electrolytes will be assumed to be completely dissociated, and no correction for activity coefficients will be made.

I, 13. Dissociation of Polybasic Acids.—When a polybasic acid is dissolved in water, the various hydrogen atoms undergo dissociation to different extents. For a *dibasic acid* H_2A, the primary and secondary dissociation can be represented by the equations:

$$H_2A \rightleftharpoons H^+ + HA^- \qquad (1);$$

$$HA^- \rightleftharpoons H^+ + A^{--} \qquad (2).$$

If the dibasic acid is a weak electrolyte, the law of mass action may be applied, and the following expressions obtained:

$$[H^+] \times [HA^-]/[H_2A] = K_1 \qquad (1A),$$

$$[H^+] \times [A^{--}]/[HA^-] = K_2 \qquad (2A).$$

K_1 and K_2 are known as the *primary* and *secondary dissociation constants* respectively. Each stage of the dissociation process has its own ionisation constant, and the magnitudes of these constants give a measure of the extent to which each ionisation has proceeded at any given concentration. The greater the value of K_1 relative to K_2, the smaller will be the secondary dissociation, and the greater must be the dilution before the latter becomes appreciable. It is therefore possible that a dibasic (or polybasic) acid may behave, so far as dissociation is concerned, as a monobasic acid over a considerable concentration range. This is indeed characteristic of many polybasic acids (see Table VI).

A *tribasic acid* H_3A (*e.g.*, orthophosphoric acid) will similarly yield three dissociation constants, K_1, K_2 and K_3, which may be computed in an analogous manner:

$$H_3A \rightleftharpoons H^+ + H_2A^- \qquad (3);$$
$$H_2A^- \rightleftharpoons H^+ + HA^{--} \qquad (4);$$
$$HA^{--} \rightleftharpoons H^+ + A^{---} \qquad (5).$$

We can now apply some of the theoretical considerations to actual examples encountered in qualitative analysis.*

Example 1. To calculate the concentrations of HS^- and S^{--} in a saturated solution of hydrogen sulphide.

A saturated aqueous solution of hydrogen sulphide at 25°, at atmospheric pressure, is approximately 0·1 molar. The primary and secondary dissociation constants are $9{\cdot}1 \times 10^{-8}$ and $1{\cdot}2 \times 10^{-15}$ respectively.

$$\text{Thus } [H^+] \times [HS^-] \;/\; [H_2S] = 9{\cdot}1 \times 10^{-8} \qquad \text{(i)},$$
$$\text{and } [H^+] \times [S^{--}] \;/\; [HS^-] = 1{\cdot}2 \times 10^{-15} \qquad \text{(ii)}.$$

The very much smaller value of K_2 indicates that the secondary dissociation, and consequently $[S^{--}]$ is exceedingly small. It follows, therefore, that only the primary ionisation is of importance, and $[H^+]$ and $[HS^-]$ are practically equal in value. Substituting in equation (i): $[H^+] = [HS^-]$ and $[H_2S] = 0{\cdot}1$, one obtains $[H^+] = [HS^-] = \sqrt{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1} = 9{\cdot}5 \times 10^{-5}$.

Both the equilibrium equations must be satisfied simultaneously; by substitution of these values for $[H^+]$ and $[HS^-]$ in equation (ii) one obtains $9{\cdot}5 \times 10^{-5} \times [S^{--}] = 1{\cdot}2 \times 10^{-15} \times 9{\cdot}5 \times 10^{-5}$, or $[S^{--}] = 1{\cdot}2 \times 10^{-15}$, which is the value for K_2.

If one multiplies equations (i) and (ii) together and transposes:

$$[S^{--}] = 1{\cdot}1 \times 10^{-23} \;/\; [H^+]^2.$$

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen ion concentration, *i.e.*, if one, say, doubles $[H^+]$ by the addition of a strong acid, the $[S^{--}]$ would be reduced to $1/2^2$ or 1/4 of its original value.

I, 14. Common Ion Effect.—The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound which produces that ion upon dissociation. The particular ion is thus derived from the compound already in solution and from the added reagent, hence the name *common ion*. We shall confine our attention to the case in which the original compound is a weak electrolyte in order that the law of mass action may be applicable. The result is usually that there is a higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced. Examples of the calculation of the common ion effect are given below. In general, it may be stated that if the total concentration of the common ion is only slightly larger than that which the original compound alone would furnish, the effect is small; if, however, the concentration of the common ion is very much increased (*e.g.*, that produced by the addition of a completely dissociated salt), the effect is very great and may be of considerable practical importance. Indeed, the common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

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* For further examples the reader is referred to any of the numerous books on chemical calculations.

Example 2. To calculate the sulphide ion concentration in a 0·25 molar hydrochloric acid solution saturated with hydrogen sulphide.

This concentration has been chosen since it is that at which the sulphides of the metals of Group II are precipitated. The total concentration of hydrogen sulphide will be approximately the same as in aqueous solution, *i.e.* 0·1 *M*; the $[H^+]$ will be equal to that of the completely dissociated HCl, *i.e.* 0·25 *M*, but the $[S^{--}]$ will be reduced below $1{\cdot}2 \times 10^{-15}$.

Substituting in equations (i) and (ii) (Section **I, 13**), one finds:

$$[HS^-] \quad \frac{9{\cdot}1 \times 10^{-8} \times [H_2S]}{[H^+]} = \frac{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1}{0{\cdot}25} = 3{\cdot}6 \times 10^{-8},$$

$$[S^{--}] = \frac{1{\cdot}2 \times 10^{-15} \times [HS^-]}{[H^+]} = \frac{1{\cdot}2 \times 10^{-15} \times 3{\cdot}6 \times 10^{-8}}{0{\cdot}25}$$

$$= 1{\cdot}7 \times 10^{-22}.$$

Thus by changing the acidity from $9{\cdot}5 \times 10^{-5}$ *M* (that present in saturated H_2S water) to 0·25 *M*, the sulphide ion concentration is reduced from $1{\cdot}2 \times 10^{-15}$ to $1{\cdot}7 \times 10^{-22}$.

Example 3. What effect has the addition of 0·1 gram molecule (8·20 grams) of anhydrous sodium acetate to 1 litre of 0·1 molar acetic acid upon the degree of ionisation of the acid?

The dissociation constant of acetic acid at 25° is $1{\cdot}82 \times 10^{-5}$. The degree of dissociation α in 0·1 *M* solution ($c = 0{\cdot}1$) may be computed by solving the quadratic equation:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{\alpha^2 c}{(1 - \alpha)} = 1{\cdot}82 \times 10^{-5}.$$

For our purpose it is sufficiently accurate to neglect α in $(1-\alpha)$, since α is small:

$$\therefore \alpha = \sqrt{K/c} = \sqrt{1{\cdot}82 \times 10^{-4}} = 0{\cdot}0135.$$

Hence in 0·1 *M* acetic acid,

$[H^+] = 0{\cdot}00135$, $[C_2H_3O_2^-] = 0{\cdot}00135$ and $[H.C_2H_3O_2] = 0{\cdot}0986$.

The concentrations of sodium and acetate ions produced by the addition of the completely dissociated sodium acetate are:

$[Na^+] = 0{\cdot}1$ and $[C_2H_3O_2^-] = 0{\cdot}1$ gram mol respectively. The acetate ions from the salt will tend to decrease the ionisation of the acetic acid since K is constant, and consequently the acetate ion concentration derived from it. Hence we may write, $[C_2H_3O_2^-] = 0{\cdot}1$ for the solution, if α' is the new degree of ionisation,

$[H^+] = \alpha'c = 0{\cdot}1\ \alpha'$, and $[H.C_2H_3O_2] = (1-\alpha')c = 0{\cdot}1$, since α' is negligibly small.

Substituting in the mass action equation:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{0{\cdot}1\ \alpha' \times 0{\cdot}1}{0{\cdot}1} = 1{\cdot}82 \times 10^{-5},$$

$$\text{or } \alpha' = 1{\cdot}8 \times 10^{-4}.$$

$$[H^+] = \alpha'c \doteq 1{\cdot}8 \times 10^{-5}.$$

The addition of a tenth of an equivalent weight of sodium acetate to a 0·1 molar solution of acetic acid has decreased the degree of ionisation from 1·35% to 0·018%, and the hydrogen ion concentration from 0·0135 to 0·000018.

Example 4. What effect has the addition of 0·5 gram molecule (26·75 grams) of ammonium chloride to one litre of 0·1 molar ammonium hydroxide solution upon the degree of dissociation of the base?

(Dissociation constant of $NH_4OH = 1{\cdot}8 \times 10^{-5}$.)

In 0·1 *M* ammonia solution $\alpha = \sqrt{1{\cdot}8 \times 10^{-5} \times 0{\cdot}1} = 0{\cdot}013$.

Hence $[OH^-] = 0{\cdot}0013$, $[NH_4^+] = 0{\cdot}0013$ and $[NH_4OH] = 0{\cdot}0987$.

Let α' be the degree of dissociation in the presence of the added ammonium chloride. Then $[OH^-] = \alpha'c = 0{\cdot}1\alpha'$ and

$[NH_4OH] = (1-\alpha')c = 0{\cdot}1$, since α' may be taken as negligibly small. The addition of the completely ionised ammonium chloride will of necessity decrease the $[NH_4^+]$ derived from the base and increase $[NH_4OH]$, since K is constant under all conditions. Now $[NH_4^+] = 0{\cdot}5$, as a first approximation.

Substituting in the equation:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = \frac{0{\cdot}5 \times 0{\cdot}1\alpha'}{0{\cdot}1} = 1{\cdot}8 \times 10^{-5},$$

$$\text{or } \alpha' = 3{\cdot}6 \times 10^{-5} \text{ and } [OH^-] = 3{\cdot}6 \times 10^{-6}.$$

The addition of half of an equivalent weight of ammonium chloride to a 0·1 molar solution of ammonium hydroxide has decreased the degree of ionisation from 1·35% to 0·0036%, and the hydroxyl ion concentration from 0·0013 to 0·0000036.

I, 15 SOLUBILITY PRODUCT

For sparingly soluble electrolytes (*i.e.*, those of which the solubility is less than 0·01 gram molecules per litre) it is an experimental fact that the product of the total molar concentrations of the ions is a constant at constant temperature. This product S is termed the *solubility product.* For a binary electrolyte :

$$AB \rightleftharpoons A^+ + B^-,$$
$$S_{AB} = [A^+] \times [B^-].$$

In general, for an electrolyte A_pB_q, which ionises into $pA^{+\cdots\cdot}$ and $qB^{-\cdots\cdot}$ ions :

$$A_pB_q \rightleftharpoons pA^{+\cdots\cdot} + qB^{-\cdots\cdot},$$
$$S_{A_pB_q} = [A^{+\cdots\cdot}]^p \times [B^{-\cdots\cdot}]^q.$$

This relationship can be readily deduced as follows. For simplicity, consider a binary electrolyte :

$$AB \rightleftharpoons A^+ + B^-.$$

The solid is completely ionised in dilute solution ; no unionised molecules will therefore be present. It can be shown by thermodynamics that in a saturated solution of any salt containing varying amounts of a more soluble salt with a common ion, the products of the activities of the two ions in the various saturated solutions are the same :

i.e. $a_{A^+} \times a_{B^-}$ constant.

In the very dilute solutions with which we are here concerned, the activities may be taken as practically equal to the concentration,* so that $[A^+] \times [B^-] = \text{constant}$.

Some experimental results, due to Jahn 1904, illustrating the constancy of the solubility product of silver chloride in the presence of varying concentrations of chloride ions (from potassium chloride) are collected in Table VII.

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* Activity = activity coefficient × concentration, *i.e.*, $a = fc$. The solubility product equation may therefore be written :

$$(f_{A^+} \times [A^+] (f_{B^-} \times [B^-]) = \text{constant}.$$

In very dilute solution f is proportional to $(1 - k\sqrt{c})$, and if c is small, this quantity is approximately unity.

TABLE VII. EFFECT OF CHLORIDE IONS UPON THE SOLUBILITY PRODUCT OF AgCl.

$[KCl]$	$[Cl^-] \times 10^3$	$[Ag^+] \times 10^8$	$S_{AgCl} = [Ag^+].[Cl^-] \times 10^{10}$
0·00670	6·4	1·75	1·12
0·00833	7·9	1·39	1·10
0·01114	10·5	1·07	1·12
0·01669	15·5	0·74	1·14
0·03349	30·3	0·39	1·17

It is important to note that the solubility product relation applies only to saturated solutions of slightly soluble electrolytes and with *small* additions of other salts. In the presence of large concentrations of salts, the ionic concentration, and therefore the ionic strength of the solution, will increase. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant. However, the presence of foreign salts up to a concentration of about 0·2—0·3 molar is without considerable influence upon the solubility product.

The great importance of the conception of solubility product lies in its bearing upon precipitation from solution, which is, of course, one of the principal operations of qualitative analysis. The solubility product is the ultimate value which is attained by the ionic product when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution. If the experimental conditions are such that the ionic product is different from the solubility product, then the system will attempt to adjust itself in such a manner that the ionic and solubility products are equal in value. Thus, if, for a given electrolyte, the product of the concentrations of the ions in solution is arbitrarily made to exceed the solubility product, as for example by the addition of a salt with a common ion, the adjustment of the system results in the precipitation of the solid salt, provided supersaturation conditions are excluded. If the ionic product is less than the solubility product or can arbitrarily be made smaller, as for example by complex salt formation or by the formation of weak electrolytes (see Sect. **I, 20**), then a further quantity of the solute can pass into solution until the solubility product is attained, or if this is not possible, until all the solute has dissolved.

TABLE VIII. SOLUBILITY PRODUCTS AT THE LABORATORY TEMPERATURE.

Substance.	*Solubility Product.*	*Substance.*	*Solubility Product.*
AgBr	$3{\cdot}5 \times 10^{-13}$	FeS	$1{\cdot}5 \times 10^{-19}$
AgCNS	$7{\cdot}1 \times 10^{-13}$	Hg_2Br_2	$1{\cdot}3 \times 10^{-18}$
AgCl	$1{\cdot}2 \times 10^{-10}$	Hg_2Cl_2	$2{\cdot}0 \times 10^{-21}$
Ag_2CrO_4	$1{\cdot}7 \times 10^{-12}$	Hg_2I_2	$1{\cdot}2 \times 10^{-28}$
AgI	$1{\cdot}7 \times 10^{-16}$	HgS	4×10^{-53}
Ag_3PO_4	$1{\cdot}8 \times 10^{-18}$	$KHC_4H_4O_6$	$3{\cdot}0 \times 10^{-4}$
Ag_2S	$1{\cdot}6 \times 10^{-49}$	K_2PtCl_6	$4{\cdot}9 \times 10^{-5}$
$Al(OH)_3$	$8{\cdot}5 \times 10^{-23}$	$MgCO_3$	$2{\cdot}6 \times 10^{-5}$
$BaCO_3$	$1{\cdot}9 \times 10^{-9}$	MgC_2O_4	$8{\cdot}6 \times 10^{-5}$
BaC_2O_4	$1{\cdot}7 \times 10^{-7}$	MgF_2	$7{\cdot}0 \times 10^{-9}$
$BaCrO_4$	$2{\cdot}3 \times 10^{-10}$	$Mg(NH_4)PO_4$	$2{\cdot}5 \times 10^{-13}$
$BaSO_4$	$1{\cdot}2 \times 10^{-10}$	$Mg(OH)_2$	$1{\cdot}5 \times 10^{-11}$
$CaCO_3$	$1{\cdot}7 \times 10^{-8}$	$Mn(OH)_2$	$4{\cdot}0 \times 10^{-14}$
CaC_2O_4	$3{\cdot}8 \times 10^{-9}$	MnS	$1{\cdot}4 \times 10^{-15}$
$CaC_4H_4O_6$		$Ni(OH)_2$	$8{\cdot}7 \times 10^{-19}$
(tartrate)	$7{\cdot}7 \times 10^{-7}$	NiS	$1{\cdot}4 \times 10^{-24}$
CaF_2	$3{\cdot}2 \times 10^{-11}$	$PbBr_2$	$7{\cdot}9 \times 10^{-5}$
$CaSO_4$	$2{\cdot}3 \times 10^{-4}$	$PbCl_2$	$2{\cdot}4 \times 10^{-4}$
CdS	$3{\cdot}6 \times 10^{-29}$	$PbCO_3$	$1{\cdot}7 \times 10^{-11}$
$Co(OH)_2$	$1{\cdot}6 \times 10^{-18}$	$PbCrO_4$	$1{\cdot}8 \times 10^{-14}$
CoS	$1{\cdot}9 \times 10^{-27}$	PbF_2	$7{\cdot}0 \times 10^{-9}$
$Cr(OH)_3$	$2{\cdot}9 \times 10^{-29}$	PbI_2	$1{\cdot}4 \times 10^{-8}$
$Cu_2(CNS)_2$	$1{\cdot}7 \times 10^{-11}$	PbS	$4{\cdot}2 \times 10^{-28}$
Cu_2Br_2	$4{\cdot}1 \times 10^{-8}$	$PbSO_4$	$2{\cdot}3 \times 10^{-8}$
Cu_2Cl_2	$1{\cdot}4 \times 10^{-6}$	$SrCO_3$	$4{\cdot}6 \times 10^{-9}$
Cu_2I_2	$2{\cdot}6 \times 10^{-12}$	SrC_2O_4	$1{\cdot}4 \times 10^{-7}$
CuS	$8{\cdot}5 \times 10^{-45}$	$SrSO_4$	$3{\cdot}6 \times 10^{-7}$
$Fe(OH)_2$	$1{\cdot}6 \times 10^{-14}$	$Zn(OH)_2$	$1{\cdot}0 \times 10^{-18}$
$Fe(OH)_3$	$1{\cdot}1 \times 10^{-36}$	ZnS	*ca.* 1×10^{-20}

The concentrations are expressed in gram mols per litre for the calculation of solubility products. A few examples may help the student to fully understand the subject.

Example 5. The solubility of silver chloride is 0·0015 grams per litre. Calculate the solubility product.

The molecular weight of AgCl is 143·5.

The solubility is therefore $0{\cdot}0015/143{\cdot}5 = 1{\cdot}05 \times 10^{-5}$ mols per litre. In a saturated solution the dissociation, $AgCl \rightleftharpoons Ag^+ + Cl^-$, is complete; 1 mol of AgCl will give 1 mol each of Ag^+ and Cl^-. Hence $[Ag^+] = 1{\cdot}05 \times 10^{-5}$ and $[Cl^-] = 1{\cdot}05 \times 10^{-5}$.

$$S_{AgCl} = [Ag^+] \times [Cl^-] = (1{\cdot}05 \times 10^{-5}) \times (1{\cdot}05 \times 10^{-5}) = \mathit{1{\cdot}1 \times 10^{-10}}.$$

Example 6. Calculate the solubility product of silver chromate, given that its solubility is $2{\cdot}5 \times 10^{-2}$ grams per litre.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{--}.$$

The molecular weight of Ag_2CrO_4 is 332, hence the solubility $= 2{\cdot}5 \times 10^{-2}/332 = 7{\cdot}5 \times 10^{-5}$ mols per litre.

Now 1 mol of Ag_2CrO_4 gives two mols of Ag^+ and 1 mol of CrO_4^{--},

$$\begin{aligned} \text{therefore } S_{Ag_2CrO_4} &= [Ag^+]^2 \times [CrO_4^{--}] \\ &= (2 \times 7{\cdot}5 \times 10^{-5})^2 \times (7{\cdot}5 \times 10^{-5}) \\ &= \mathit{1{\cdot}7 \times 10^{-12}}. \end{aligned}$$

In order to explain many of the reactions of qualitative analysis in a clear and intelligible manner, the values of the solubility products of the various sparingly soluble substances are useful. Some of the most important figures are collected in Table VIII, which is extracted largely from the literature. The student is referred to text-books on physical chemistry for a description of the methods for determining these quantities. It must, however, be pointed out that the various methods do not always yield consistent results, and what appear to be the best representative figures are therefore given in the Table.

I, 16. Application of the Solubility Product Relation.—*Precipitation of Sulphides.* The solubility products of a number of common sulphides are: HgS 4×10^{-53}, PbS $4{\cdot}2 \times 10^{-28}$, CuS $8{\cdot}5 \times 10^{-45}$, CdS $3{\cdot}6 \times 10^{-29}$, MnS $1{\cdot}4 \times 10^{-15}$ and ZnS 1×10^{-20}. When hydrogen sulphide is passed into a solution of the salts of these metals, precipitation will occur when $[M^{++}] \times [S^{--}]$ exceeds the solubility product (M^{++} is the ion of the metal). In the usual course of qualitative analysis, the concentration of the metallic ions cannot be varied between wide limits since one is limited, on the one hand, by the solubility of the salt and, on the other hand, by the necessity of obtaining sufficient precipitate to handle and to use for qualitative tests. The concentration of the solution is of the order 10^{-1} to 1 molar. The sulphide ion concentration can, however, be varied between wide limits. We have already seen that in 0·25 molar hydrochloric acid (Sect. **I, 13,** *Example* 2), the concentration at which Group II is usually precipitated, $[S^{--}]$ is $1{\cdot}7 \times 10^{-22}$; under these conditions only the solubility products of HgS, PbS, CuS and CdS are exceeded, and these are therefore almost completely precipitated.* If the concentration of the acid is much higher, then $[S^{--}]$ is reduced still further, and it is not difficult to see that CdS will be either not precipitated at all or incompletely precipitated. In a saturated aqueous solution of hydrogen sulphide, $[S^{--}]$ is 1×10^{-15}, and under these conditions ZnS is partially precipitated; precipitation ceases at a certain concentration, due to the accumulation of hydrogen ions arising from the acid produced in the reaction. The increased hydrogen ion concentration decreases the dissociation of the hydrogen sulphide until $[S^{--}]$ is such that $[Zn^{++}] \times [S^{--}]$ is not in excess of the solubility product. For the complete precipitation of zinc sulphide, the hydrogen ions must be removed or their concentration considerably reduced; this can be achieved by the addition of sodium acetate. The latter gives rise to the feebly dissociated acetic acid ($C_2H_3O_2^- + H^+ \rightleftharpoons H.C_2H_3O_2$), the $[S^{--}]$ is maintained sufficiently high and precipitation is complete. Another method is to employ a soluble sulphide, *e.g.*, ammonium sulphide, which gives a high concentration of sulphide ions in solution; ZnS, MnS and related sulphides can then be completely precipitated.

Example 7. Calculate the maximum concentration of Cd^{++} ions and of Mn^{++} ions which will remain in solution after precipitation by excess of H_2S in 0·25 *M* HCl. (Solubility products: CdS = $3{\cdot}6 \times 10^{-29}$; MnS = $1{\cdot}4 \times 10^{-15}$.)

The sulphide ion concentration $[S^{--}]$ in 0·25 *M* HCl saturated with H_2S is $1{\cdot}7 \times 10^{-22}$ gram mol per litre.

Now $[Cd^{++}] \times [S^{--}] = 3{\cdot}6 \times 10^{-29}$;

$\therefore$ $[Cd^{++}] = 3{\cdot}6 \times 10^{-29}/1{\cdot}7 \times 10^{-22} = 2{\cdot}1 \times 10^{-7}$ gram mol per litre.

$= 2{\cdot}1 \times 10^{-7} \times 112{\cdot}4 = 2{\cdot}4 \times 10^{-5}$ grams per litre.

The solution will thus contain 0·024 mgm. Cd^{++} ions per litre—a negligible quantity.

For manganese sulphide, $[Mn^{++}] \times [S^{--}] = 1{\cdot}4 \times 10^{-15}$;

$\therefore$ $[Mn^{++}] = 1{\cdot}4 \times 10^{-15}/1{\cdot}7 \times 10^{-22} = 8{\cdot}2 \times 10^{6}$ gram mol per litre,

$= 8{\cdot}2 \times 10^{6} \times 55 = 4{\cdot}5 \times 10^{8}$ grams per litre.

This figure clearly shows that no MnS will be precipitated in 0·25 *M* HCl solution.

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* A detailed calculation is given at the end of this paragraph to illustrate this point.

Precipitation of Hydroxides.—Here also the hydroxyl ion concentration of the precipitating agent is controlled, and the method is employed to differentiate between hydroxides of different solubility products. We have seen (Section **I, 13,** *Example 4*) that the addition of ammonium chloride to ammonia solution* reduces the hydroxyl ion concentration considerably. The resultant $[OH^-]$ is sufficient to exceed the solubility products of iron, aluminium and chromium but not of cobalt, nickel, manganese, zinc and magnesium hydroxides; the latter therefore remain in solution, whilst the former are precipitated when ammonium chloride and ammonia solution are added to a solution of their salts.

A very instructive example of the application of the solubility product principle is the *precipitation and solution of aluminium hydroxide.* The addition of hydroxyl ions in the form of sodium, potassium or ammonium hydroxides to a solution of an aluminium salt yields a white gelatinous precipitate of aluminium hydroxide, which possesses amphoteric properties. It will dissolve in solutions of caustic alkalis forming solutions of alkali aluminates, and also in solutions of acids forming the aluminium salts of the acids. The dissociation of aluminium hydroxide in aqueous solution may be expressed:

$$(c)\ Al^{+++} + 3OH^- \rightleftharpoons Al(OH)_3 \begin{array}{l} \nearrow\!\!\!\swarrow H_3AlO_3 \rightleftharpoons AlO_3^{---} + 3H^+ \qquad (a) \\ \searrow\!\!\!\nwarrow H_2O + HAlO_2 \rightleftharpoons AlO_2^- + H^+ + H_2O \ (b) \end{array}$$

Basic dissociation *Acid dissociation.*

The acid dissociation (*b*) is commonly accepted as taking place to a very much greater extent than (*a*), particularly in strongly alkaline solution, since the solid salt $NaAlO_2$ and not Na_3AlO_3 has been isolated by direct evaporation of the solution in sodium hydroxide. We shall therefore regard the dissociation (*a*) as being negligible.

Let us now consider what will happen when excess of a strong acid, *i.e.*, H^+ ions, is added to a suspension of aluminium hydroxide. The acid dissociation (*b*) would be repressed on account of the common ion effect, and the basic dissociation (*c*) would be simultaneously enhanced, due to the combination of the H^+ ions with the OH^- ions of the solution to form undissociated water. Initially, the ionic product of water, $[H^+] \times [OH^-] = 1 \times 10^{-14}$, held, but with the addition of excess of H^+ ions, *i.e.*, with a large increase of $[H^+]$, this will be momentarily greatly exceeded. In order that the ionic product relation for water be maintained under the new experimental conditions, it will be necessary for the hydroxyl ions supplied by the aluminium hydroxide to combine with the hydrogen ions of the acid to form water. The removal of hydroxyl ions in this manner will necessitate the further dissociation of the aluminium hydroxide according to (*c*) since the solubility product relation

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* The terms ammonia solution and ammonium hydroxide solution are used synonymously throughout this book and refer, of course, to the aqueous solution of ammonia.

$$[Al^{+++}] \times [OH^-]^3 = S_{Al(OH)_3}$$

(the latter is very small) must hold simultaneously. Since $[H^+]$ is very large, the further dissociation and consequent solution of the aluminium hydroxide will continue until the latter is completely dissolved.

The addition of a solution of a strong base, sodium or potassium hydroxide, *i.e.*, of a large hydroxyl ion concentration, will similarly repress the basic dissociation (*c*) and increase the acid dissociation (*b*), owing to combination with the hydrogen ions derived from this dissociation. It is clear that in order to maintain the solubility product of both water and aluminium hydroxide constant under the new conditions, more $Al(OH)_3$ must dissociate in accordance with (*b*); in consequence of the high hydroxyl ion concentration this process will continue until all the aluminium hydroxide has passed into solution.

The precipitation of $Al(OH)_3$ by treating its solution in strong alkali (thus containing AlO_2^- ions) with excess of ammonium chloride solution and boiling, is readily interpreted. The effect of the large concentration of ammonium ions is to decrease the hydroxyl ion concentration as a result of the formation of the slightly ionised NH_4OH; the excess of the latter is removed by boiling as ammonia gas.

$$NH_4 + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 \uparrow + H_2O.$$

This reduction of hydroxyl ion concentration will promote the reaction (*c*) and will bring about the combination of H^+ and AlO_2^- to produce a concentration of $Al(OH)_3$ in excess of that in a saturated solution. The excess of aluminium hydroxide will then be precipitated.

I, 17. Solubility of Sparingly Soluble Salts of Weak Acids in Strong Mineral Acids.—The solubility product principle enables one to give a simple explanation of this phenomenon, which is of relatively frequent occurrence in qualitative

These two expressions and also the relation :

$$\frac{[Sr^{++}]}{[Ba^{++}]} = \frac{3{\cdot}6 \times 10^{-7}}{1{\cdot}2 \times 10^{-10}} = \frac{3000}{1} \qquad \text{(vi)},$$

must be satisfied for equilibrium between the two precipitates. It follows therefore :

(*a*) if $[Sr^{++}] > 3000\ [Ba^{++}]$, and SO_4^{--} is added, $SrSO_4$ will be precipitated until $[Sr^{++}] = 3000\ [Ba^{++}]$;

(*b*) if $Sr^{++} < 3000\ [Ba^{++}]$, and SO_4^{--} is added, $BaSO_4$ will be precipitated until $[Sr^{++}] = 3000\ [Ba^{++}]$.

Further addition of SO_4^{--} in either (*a*) or (*b*) will result in the precipitation of a mixture of $SrSO_4$ and $BaSO_4$ in the ratio of 3000 to 1, the equilibrium ratio (vi) in the supernatant liquid being maintained.

The student should carry out a similar calculation for $SrSO_4$ and $CaSO_4$ (solubility product $= 2{\cdot}3 \times 10^{-4}$) : this has an important bearing upon the separation of Group IV metals (see Sections **III, 32** and **V, 15**).

I, 19. Preparation of Solutions.—In order to prepare a " solution " of a substance sparingly soluble in water, the process of precipitation must be reversed, *i.e.*, the action of the reagent must be such as to reduce the concentration of one or both of the ions of the slightly soluble substance. The concentration of an ion can be reduced by one of the following methods : (*a*) the formation of a weak electrolyte or of undissociated molecules ; (*b*) the formation of a complex ion ; (*c*) by double decomposition ; and (*d*) by oxidation or reduction.

The first method is applicable to electrolytes which are derivatives of weak acids (or bases), such as barium sulphite, calcium phosphate, calcium carbonate and ferrous sulphide. If any of these substances is treated with dilute hydrochloric acid, solution occurs because of the formation of the weak acids H_2SO_3, $H_2PO_4^-$, H_2CO_3 and H_2S. These weak electrolytes can exist in equilibrium with only a very small concentration of their ions, and the anion concentration is diminished still further by the presence of hydrogen ions from the completely dissociated hydrochloric acid. The ionic concentration is thus reduced to so low a value that the solubility product is never exceeded, and the substance passes into solution in an attempt to restore the solubility product equilibrium. Let us consider a particular case in detail—

the solution of ferrous sulphide in dilute hydrochloric acid. The ionic equilibria involved will be :

$FeS \rightleftharpoons Fe^{++} + S^{--}$ (solubility product $= 1{\cdot}5 \times 10^{-19}$) (i) ;

$HCl \rightleftharpoons H^{+} + Cl^{-}$ (ii)

$2H^{+} + S^{--} \rightleftharpoons H_2S$

(*or* $H^{+} + S^{--} \rightleftharpoons HS^{-} + H^{+} \rightleftharpoons H_2S$) (iii), and

$Fe^{++} + 2Cl^{-} \rightleftharpoons FeCl_2$ (iv).

The hydrochloric acid is completely dissociated ; the concentration of HCl must therefore be regarded as infinitesimally small. Combination between the H^{+} from the acid and the S^{--} gives the weakly ionised and slightly soluble gas H_2S ; that in excess of the solubility of the latter will be evolved as the free gas. The sulphide ion concentration is thus reduced, the equilibrium (i), controlled by

$$[Fe^{++}] \times [S^{--}] = 1{\cdot}5 \times 10^{-19},$$

is disturbed. More ferrous sulphide must therefore pass into solution to restore the reduced sulphide ion concentration, but since the latter is being continually removed by the high hydrogen ion concentration, the ultimate result will be, if the acid concentration is sufficiently great, that all the ferrous sulphide will pass into solution.

The solubility of lead sulphate in saturated ammonium acetate solution is due to the formation of the feebly ionised lead acetate. Further, manganous, zinc and magnesium hydroxides dissolve in ammonium chloride solution owing to the formation of the weak base, ammonium hydroxide.

Numerous examples are available to illustrate method (*b*), but only two will be mentioned now as the subject is treated fully in Section **I, 20.** Silver chloride is soluble in ammonia solution, due to the formation of the complex ion $[Ag(NH_3)_2]^{+}$; this yields so small a silver ion concentration, particularly in the presence of excess of ammonia solution, that the solubility product of silver chloride is not attained. In a similar manner silver cyanide dissolves in potassium cyanide solution, the complex ion $[Ag(CN)_2]^{-}$ being formed.

In method (*c*), the product of the reaction is either another insoluble substance or a substance which can be removed from the system by virtue of some such property as ease of decomposition or volatility. This procedure is exemplified when an insoluble salt is heated with a large excess of a saturated solution of sodium carbonate. Partial decomposition ensues with the formation of the insoluble carbonate of the cation and a solution containing the anion, together with the excess of carbonate ions. After filtration, the residue may be dissolved in dilute hydrochloric acid, and a solution, containing the cations, obtained. A specific example is the preparation of a solution of barium sulphate; the initial aqueous extract contains the sulphate ions, and the hydrochloric acid extract the barium ions.

Process (*d*) may be illustrated by the dissolution of cupric sulphide in nitric acid. The sulphide ion S^{--} is oxidised to free sulphur S°, the sulphide ion concentration is thereby reduced below the solubility product of CuS and hence the latter passes into solution.

I, 20. Complex Ions.—Reference was made in the previous section to the increase of solubility produced by the formation of complex ions. A *complex ion* is formed by the union of a simple ion with either other ions of opposite charge or with neutral molecules. Let us now examine a few examples in some detail.

When potassium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide is formed because the solubility product of silver cyanide,

$$[Ag^{+}] \times [CN^{-}] = S_{AgCN} \qquad \text{(i)},$$

is exceeded. The reaction is expressed:

$$K^{+} + CN^{-} + Ag^{+} + NO_3^{-} = AgCN + K^{+} + NO_3^{-},$$

$$\textit{or} \qquad CN^{-} + Ag^{+} = AgCN.$$

This precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion $[Ag(CN)_2]^{-}$ being produced:

$$\underset{\text{solid}}{AgCN} \rightleftharpoons Ag^{+} + CN^{-} + CN^{-} \rightleftharpoons [Ag(CN)_2]^{-}*$$

$$(\textit{or}\ AgCN + KCN = K[Ag(CN)_2]\text{—a soluble complex salt}).$$

This complex ion dissociates to give silver ions, since the addition of sulphide ions yields a precipitate of silver sulphide (solubility product $1{\cdot}6 \times 10^{-49}$), and also silver is deposited from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:

$$[Ag(CN)_2]^{-} \rightleftharpoons Ag^{+} + 2CN^{-} \qquad \text{(ii)}.$$

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* It is usual to employ square brackets to include the whole of a complex ion. In order to avoid confusion with concentrations for which square brackets are also widely used, concentrations will be expressed in heavy type and complex ions either in lighter type or between curly brackets.

By applying the law of mass action to (ii), one obtains the dissociation constant or *instability constant* of the complex ion :

$$\frac{[Ag^+] \times [CN^-]^2}{[\{Ag(CN)_2\}^-]} = K \qquad \text{(iii)}.$$

The constant has a value of $1{\cdot}0 \times 10^{-21}$ at the ordinary temperature. By inspection of this expression, and bearing in mind that an excess of cyanide ions is present, it should be evident that the silver ion concentration must be very small, so small in fact, that the solubility product of silver cyanide is not exceeded.

The process of solution of the silver cyanide in the potassium cyanide solution may be pictured as follows. Equations (i) and (iii) control the silver ion concentrations in AgCN and the complex $[Ag(CN)_2]^-$ respectively, the former being very much greater than the latter. The concentration of silver ions derived from the saturated solution of AgCN is much greater than that permitted by equilibrium (ii) ; accordingly, the excess of silver ions combine with cyanide ions to form the complex $[Ag(CN)_2]^-$. This will result in the lowering of the solubility product of AgCN, and more of the latter will pass into solution in order to supply the silver ions removed in the formation of the slightly dissociated complex ion. This process will continue either until all the AgCN has dissolved or until practically the whole of the CN^- has reacted to form $[Ag(CN)_2]^-$. It must be remembered that the complex salt formed, $K[Ag(CN)_2]$ is very soluble in water, and its solubility product is therefore never exceeded under the ordinary experimental conditions. This mechanism, *viz.*, the formation of a feebly dissociated complex ion from one of the ions of a completely dissociated, sparingly soluble salt and another ion or neutral molecule is the basis of all the reactions of the type that are being considered.

Consider now the solubility of silver chloride in ammonia solution. The reactions are :

$$Ag^+ + Cl^- \rightleftharpoons AgCl\,;$$

$$\underset{\text{solid}}{AgCl} \rightleftharpoons Ag^+ + Cl^- + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-,$$

$$(\textit{or}\ AgCl + 2NH_3 = [Ag(NH_3)_2]Cl).$$

Here again, for reasons similar to those already given, silver ions are present in solution. The dissociation of the complex ion is represented by :

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2\,NH_3,$$

and the instability constant is given by :

$$\frac{[Ag^+] \times [NH_3]^2}{[\{Ag(NH_3)_2\}^+]} = K = 6{\cdot}8 \times 10^{-8}.$$

The magnitude of the instability constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

Another familiar example is the solution of ferrous cyanide in potassium cyanide solution to yield potassium ferrocyanide or the ferrocyanide ion :

$$\underset{\text{solid}}{Fe(CN)_2} \rightleftharpoons Fe^{++} + 2CN^- + 4CN^- \rightleftharpoons [Fe(CN)_6]^{----}$$

$$(\textit{or}\ Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]).$$

The secondary dissociation of the ferrocyanide ion :

$$[Fe(CN)_6]^{----} \rightleftharpoons Fe^{++} + 6CN^-,$$

is so small that no method at present known can detect either the simple ferrous ion or the cyanide ion in solution : the complex ion is an extremely stable one.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the dissociation or instability constant. The more stable the complex, the smaller is the instability constant. When the complex ion is very stable, the common ionic reactions of the components are not shown. A few selected values of these constants at the ordinary temperature, determined by methods involving potentiometric titration, are collected in Table IX ; this is instructive and also useful for reference purposes.

TABLE IX. INSTABILITY CONSTANTS OF COMPLEX IONS

$\frac{[Ag^+] \times [NH_3]^2}{[\{Ag(NH_3)_2\}^+]}$	$6{\cdot}8 \times 10^{-8}$	$\frac{[Cd^{++}] \times [CN^-]^4}{[\{Cd(CN)_4\}^{--}]}$	$1{\cdot}4 \times 10^{-17}$
$\frac{[Ag^+] \times [S_2O_3^{--}]^2}{[\{Ag(S_2O_3)_2\}^{---}]}$	$1{\cdot}0 \times 10^{-13}$	$\frac{[Hg^{++}] \times [Cl^-]^4}{[\{HgCl_4\}^{--}]}$	$6{\cdot}0 \times 10^{-17}$
$\frac{[Ag^+] \times [CN^-]^2}{[\{Ag(CN)_2\}^-]}$	$1{\cdot}0 \times 10^{-21}$	$\frac{[Hg^{++}] \times [I^-]^4}{[\{HgI_4\}^{--}]}$	$5{\cdot}0 \times 10^{-31}$
$\frac{[Cu^+] \times [CN^-]^4}{[\{Cu(CN)_4\}^{---}]}$	$5{\cdot}0 \times 10^{-28}$	$\frac{[Hg^{++}] \times [CN^-]^4}{[\{Hg(CN)_4\}^{--}]}$	$4{\cdot}0 \times 10^{-42}$

Complex ions are formed by Cu^{++}, Cd^{++}, Ni^{++}, Co^{+++} and Zn^{++} with NH_3 molecules, *e.g.*,

$$Co^{+++} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{+++},$$

$$Zn^{++} + 6NH_3 \rightleftharpoons [Zn(NH_3)_6]^{++}.$$

Many halide complexes are known ; these include $[HgCl_4]^{--}$, $[PtCl_6]^{--}$, $[AuCl_4]^{-}$ and $[SnCl]_6^{--}$. Many of these will be referred to in the book in connexion with the reactions of the metallic ions.

Only one further example need be considered here. It is the ordinary method for the separation of Cu^{++} and Cd^{++}. A solution containing these ions is treated with excess of ammonia solution, and then with potassium cyanide solution until the blue colour of the solution is just discharged (see Section **V, 11**). The resultant solution then contains the complex salts $K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$. Reference to Table IX clearly shows that the cadmium complex is very much less stable than the cuprous complex. When hydrogen sulphide is passed into the solution CdS is precipitated (solubility product $3{\cdot}6 \times 10^{-29}$), but no copper sulphide (solubility product; Cu_2S 2×10^{-47}, CuS $8{\cdot}5 \times 10^{-45}$) in spite of the fact that the solubility product is much smaller. This illustrates the great stability of the $[Cu(CN)_4]^{---}$ ion.

CHEMICAL EQUATIONS

The two fundamental laws of chemistry, the law of definite proportions and the law of conservation of mass, find their chief expression in practice in the form of chemical formulae and balanced equations. It is therefore of great importance that the student should be familiar with the methods of writing formulae and balancing equations. If the atomic weights are known, the percentage composition of a compound can be calculated from its chemical formula ; the ratio of the weights in which substances interact and the relative weights of the products can likewise be computed from the chemical equation representing the reaction. These quantities find considerable application in the calculations of both qualitative and quantitative analysis.

I, 21. Chemical Formulae.—The important principle to be borne in mind when writing the more common chemical formulae is that the elements or radicals must be combined in equivalent proportions. Thus univalent elements or radicals combine (i) with other univalent elements or radicals in the ratio of 1 : 1, *e.g.*, NaCl, $NH_4.C_2H_3O_2$; (ii) with bivalent atoms or radicals in the ratio of 2 : 1, *e.g.*, Na_2SO_4, $CaCl_2$, $(NH_4)_2C_2O_4$; (iii) with tervalent elements or radicals in the ratio of 3 : 1, *e.g.*, $FeCl_3$, H_3PO_4 ; and (iv) with tetravalent elements or radicals in the ratio of 4 : 1, *e.g.*, $SnCl_4$, $Pb(C_2H_3O_2)_4$. Bivalent elements or radicals combine with other bivalent elements or radicals in the ratio of 1 : 1, *e.g.*, $MgSO_4$, CaC_2O_4 ; with tervalent radicals in the ratio of 3 : 2, *e.g.*, $Ca_3(PO_4)_2$, $Al_2(SO_4)_3$, *etc.* These facts are sometimes expressed in the form of the following rule, which is applicable to normal salts : divide the least common multiple of the valencies of the two ions by the valency of each ion, and use the resultant figures as subscripts to denote the ratio in which the two ions are combined in the salt. A subscript of 1 need not be inserted. Thus in ferric sulphate, the ferric ion has a valency of 3 and the sulphate ion a valency of 2. The least common multiple is 6 and the formula is therefore $Fe_2(SO_4)_3$.

This rule implies a previous knowledge of the valencies of the ions or radicals, and applies only to those salts which contain one kind of positive ion in combination with one kind of negative ion. When applied to more complex compounds, such as acid salts, basic salts and double salts, the rule must be interpreted in the form that the sum of the valencies of the positive radicals (valency multiplied by the subscript for each radical) must equal the sum of the valencies of the negative radicals. Thus in basic lead acetate, $Pb(C_2H_3O_2)_2,Pb(OH)_2$ or $Pb_2(C_2H_3O_2)_2(OH)_2$, the total valency of the lead ions is 4 and the total valency of the acetate and hydroxyl radicals is also 4. In iron alum, $(NH_4)_2SO_4,Fe_2(SO_4)_3$ or $(NH_4)Fe(SO_4)_2$, the positive and negative valencies are both 4.

I, 22. Chemical Equations.—To construct a chemical equation one must know the formulae of the reactants and of the products of the reaction ; the skeleton equation can then be written down. In order to balance the equation, the same principle as was employed in deducing the formulae of normal salts is utilised, that is, reagents interact with each other in equivalent proportions. If the latter are known, the completion of the equation is a simple matter. The difficulty, however, is in determining the number of equivalents represented by the molecular formulae of the reactants. Methods for determining these are described below.

It is convenient to divide equations into two groups (*A*) those not involving oxidation—reduction and (*B*) those that do involve oxidation—reduction (*vide infra* for definition of oxidation and reduction).

(*A*) *Equations not involving oxidation-reduction.*—The most common reaction of this class is that involving double decomposition or metathesis, *e.g.*, the precipitation of barium sulphate by the action of barium chloride solution upon sulphuric acid, or the neutralisation of nitric acid with potassium hydroxide solution. The following procedure will be found applicable to most of the examples commonly encountered :

(i) Write down the formulae of the reactants and products in the form of a skeleton equation.

(ii) Examine the formula of the main product (or of any product more complex than the rest) to determine the reactants from which its constituents are derived.

(iii) Utilise the coefficients for the corresponding reagents that will supply these components in the correct ratio.

(iv) If one of the reactants supplies components for a second product, deduce the amount required for this, and add that amount to the coefficient required in (iii).

(v) Complete the equation by inspection.

As an example we may consider the balancing of the equations :

(*a*) $FeCl_3 + K_4[Fe(CN)_6]$;
(*b*) $HgCl_2 + KI$ (excess).

In (*a*) the products are Prussian blue $Fe_4[Fe(CN)_6]_3$ and KCl. The incomplete equation is :

$$FeCl_3 + K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + KCl.$$

The formula $Fe_4[Fe(CN)_6]_3$ requires three $[Fe(CN)_6]^{---}$ and four Fe^{+++} ions, hence at least three molecules of $K_4[Fe(CN)_6]$ and four molecules of $FeCl_3$ are required for this alone. The components of the second product KCl are supplied by the two reactants, and inspection shows that the equation is balanced by using these coefficients alone :

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

In (*b*) the products are the complex salt $K_2[HgI_4]$ and KCl,

or $HgCl_2 + KI = K_2[HgI_4] + KCl$ (incomplete).

The formula $K_2[HgI_4]$ requires four atoms of iodine to one of mercury, and the formula KCl one atom of potassium to one of chlorine. The equation when written as

$$HgCl_2 + 4KI = K_2[HgI_4] + 2KCl,$$

is balanced. If this were not the case, further adjustment of the coefficients would be necessary.

(*B*) *Equations involving oxidation-reduction.*—These are considered in Sections **I, 24.** and **I, 25.**

I, 23. Discussion of Oxidation-Reduction.—The simplest and oldest conception of oxidation involves the taking up of oxygen by an element or compound, as in the conversion of Cu_2O into CuO or of FeO into Fe_2O_3. Oxygen was the typical oxidising agent. Now Cu_2Cl_2 and $FeCl_2$ bear the same relation to $CuCl_2$ and $FeCl_3$ respectively as do the corresponding oxides to one another; it is customary, therefore, to regard the conversion of Cu_2Cl_2 and $FeCl_2$ into $CuCl_2$ and $FeCl_3$ respectively as oxidations, *i.e.*, in oxidation the positive valency of an element or radical is increased.

Reduction was formerly considered to be the process by which oxygen was removed from a compound. Hydrogen was regarded as the typical reducing agent. The definition can be logically extended to the process resulting in the decrease of the positive valency of an element or radical. Thus the conversion of Fe_2O_3 into FeO, of $FeCl_3$ into $FeCl_2$, of $CuCl_2$ into Cu_2Cl_2, are examples of reduction. It is evident that the processes of oxidation and reduction are complementary; whenever one substance is oxidised, another substance must be correspondingly reduced.

Let us write the simple equation representing the oxidation of ferrous chloride by chlorine in aqueous solution:

$$2FeCl_2 + Cl_2 = 2FeCl_3,$$

or, expressed ionically, $2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$. The ferrous ion Fe^{++} is converted into the ferric ion Fe^{+++} (oxidation) and the neutral chlorine molecule into negatively charged chloride ions Cl^- (reduction). According to the electronic conception of the constitution of matter, the conversion of Fe^{++} into Fe^{+++} requires the loss of one electron, and the transformation of the neutral chlorine molecule into chloride ions necessitates the gain of two electrons. This leads to the view that, for reactions in solution, oxidation is a process involving the loss of electrons, as in

$$Fe^{++} - \epsilon = Fe^{+++},$$

and reduction is the process resulting in the gain of electrons, as in

$$Cl_2 + 2\epsilon = 2Cl^-$$

In the actual oxidation-reduction process electrons are transferred from the reducing agent to the oxidising agent.

The following are more satisfactory definitions.

Oxidation is the increase in the positive valency of an element or radical either by the addition of oxygen, or by the addition of chlorine or some other atom or radical which can constitute acid radicals or anions (electronegative radicals). Qualitative analysis is largely concerned with reactions in solution. The above definition may therefore be extended to ionic reactions and expressed in the form: *oxidation* is the process which results in the loss of one or more electrons by atoms or ions.* An *oxidising agent* is one that gains electrons and is reduced to a lower valency condition.

Reduction is the decrease in positive valency (or increase of the negative valency) either by the removal of oxygen or some electronegative atom or radical, or by the addition of an atom or radical which can constitute cations (electropositive radical). The extension of this definition to ionic reactions is: *reduction* is a process which results in the gain of one or more electrons by atoms or ions. A *reducing agent* is accordingly one that loses electrons and becomes oxidised to a higher valency condition.

Examples of oxidising agents of importance in analytical chemistry are: the halogens, potassium permanganate, potassium dichromate, nitric acid and hydrogen peroxide. Examples of reducing agents are: sulphur dioxide, hydrogen sulphide, the metals, hydrogen, stannous chloride and hydriodic acid. A detailed discussion of these is given below.

The principle referred to above, *viz.*, that reagents react with one another in equivalent proportions, is employed in balancing oxidation-reduction equations. In all oxidation-reduction processes (or *redox* processes) there will be a reactant undergoing oxidation and one undergoing reduction, since the two reactions are complementary to one another and occur simultaneously—one cannot take place without the other. The reagent undergoing oxidation is termed the reducing agent or *reductant*, and the reagent undergoing reduction is called the oxidising agent or *oxidant*. It is necessary to determine the number of equivalents represented by one molecule of the oxidising and reducing agent respectively,

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* This statement will of course apply to electrovalent compounds in the solid state, *e.g.*, the burning of sodium in chlorine:

$$2Na + Cl_2 = 2NaCl.$$

Here the electron lost by the sodium atom is taken up by the chlorine atom.

and then to assign coefficients to each such that the number of equivalents of the oxidant and of the reductant are equal. The equation can then be completed by inspection. The number of equivalents represented by one molecule of the oxidant and the reductant is determined by direct comparison. Two methods are commonly employed for this purpose; these are considered in the two sections which follow.

I, 24. The Oxidation Number Method.—This procedure was introduced by O. C. Johnson in 1880. It is a direct development of the view that oxidation and reduction are attended by changes of valency. The fundamental conception is the state of oxidation of the elements in particular compounds. Johnson expressed this by the term " positive or negative bond." Other authors have used " valence," " changes of valence," " valence number " and " oxidation number " to express the same quantity. The present writer prefers " oxidation number " (due to McAlpine and Soule) as this term is less likely to cause confusion. The quantity is not determined by reference to any theory of atomic or molecular structure, and may be regarded as a mathematical entity deduced from an examination of the formulae of the initial and final compounds in a reaction. The *oxidation number* of an element is a number which, applied to that element in a particular compound, indicates the amount of oxidation or reduction which is required to convert one atom of the element from the *free* state into that in the compound. If oxidation is necessary to effect the change, the oxidation number is positive, and if reduction is necessary, the oxidation number is negative.

The following rules apply to the *determination of oxidation numbers* :—

(1) The oxidation number of the free or uncombined element is zero. This may be written S°, Ba°, Cl_2°, *etc.*

(2) The oxidation number of hydrogen in combination is, with few exceptions, $+1$ ($\overset{+1}{\text{H}}$).

(3) The oxidation number of oxygen in combination is normally -2 ($\overset{-2}{\text{O}}$).

(4) The oxidation number of a metal in combination is usually positive. Exception are to be found in the compounds with hydrogen, *e.g.*, $\overset{-3}{\text{Sb}}\overset{+3}{\text{H}}_3$.

(5) The oxidation number of a radical or an ion is that of its electrovalency.

(6) The oxidation number of a compound is always zero, and is determined by the sum of the oxidation numbers of the individual atoms each multiplied by the number of atoms of the element in one molecule.

Consider a few simple applications of these rules.

(i) *Oxidation number of Cu in CuO.* To convert Cu° into CuO, the copper undergoes two units of oxidation, hence the oxidation number of the copper is $+2$. Alternatively, by rule 6, since oxygen is -2, copper in $\overset{+2}{Cu}\overset{-2}{O}$ must be $+2$.

(ii) *S in H_2S.* Here $H_2 = +2$, hence S is -2.

(iii) *N in NH_4Cl.* Consider NH_3 : H_3 is $+3$, hence N is -3. In HCl, $H = +1$, therefore Cl is -1. When NH_3 and HCl combine to form NH_4Cl, the oxidation numbers of the elements in the new compound remain the same. In NH_4Cl, $H_4 = +4$ and $Cl = -1$, hence $N = -3$.

(iv) *N in HNO_3.* Here $O_3 = -6$, $H = +1$, therefore $N = +5$.

(v) *Mn in $KMnO_4$.* Here $O_4 = -8$, $K = +1$, hence $Mn = +7$.

(vi) *S in SO_4^{--}.* Here $O_4 = -8$, $SO_4^{--} = -2$, hence $-2 = -8 + S$, or $S = +6$.

(vii) *C in CO_2.* Here $O_2 = -4$, hence $C = +4$.

(viii) *C in CH_4.* Here $H_4 = +4$, hence $C = -4$.

The following rules apply to the use of the oxidation number method for the balancing of equations :

(1) Determine the numerical change in oxidation number of a significant element in the oxidant.

(2) Repeat this for a corresponding significant element in the reductant.

(3) Multiply each by coefficients which will make the total change in oxidation number equal.

(4) Inspect the skeleton equation deduced from (3), and introduce the proper coefficients for the compounds or radicals which are not oxidised or reduced.

The application to a number of examples is given below.

Reaction I : action of nitric acid upon cadmium sulphide.

$CdS + HNO_3 = Cd(NO_3)_2 + NO + S + H_2O$ (incomplete).

Nitric acid : HNO_3 : O.N.* of $N = -(-6 + 1) = +5$.

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*The term oxidation number is abbreviated to O.N.

Nitric oxide NO : O.N. of N = − (−2) = +2, *i.e.*, in the reaction nitrogen changes in O.N. from +5 to +2, or by 3 units of reduction.

Cadmium sulphide CdS : O.N. of S = − (+2) = −2.

Free sulphur : O.N. = O.

Since one molecule of HNO_3 undergoes 3 units of reduction and one molecule of CdS 2 units of oxidation, the two must react in the ratio of three molecules of CdS to two molecules of HNO_3. Furthermore, $Cd(NO_3)_2$ requires two nitrate radicals for each atom of cadmium ; six more molecules of HNO_3 will therefore be required to balance the equation. The latter will be :

$$3CdS + 8HNO_3 = 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O.$$

Reaction II : the reduction of potassium permanganate by ferrous sulphate in the presence of dilute sulphuric acid.

$$KMnO_4 + FeSO_4 + H_2SO_4 = K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O \text{ (incomplete).}$$

The oxidant $KMnO_4$ is reduced to $MnSO_4$:

$\overset{+1+7-8}{KMnO_4} \rightarrow \overset{+2+6-8}{MnSO_4}$, *i.e.*, the change in O.N. of manganese is from +7 to +2, or by 5 units of reduction.

The reductant $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$:

$\overset{+2}{Fe}(\overset{-2}{SO_4}) \rightarrow \overset{+6}{Fe_2}(\overset{-6}{SO_4})_3$, *i.e.*, the change in O.N. of one atom of iron is from +2 to 1/2 (+6), or by 1 unit of oxidation.

The $KMnO_4$ and $FeSO_4$ will therefore react in the ratio of 5 : 1. Now $Fe_2(SO_4)_3$ contains two atoms of iron ; the numbers of molecules in the ratio must accordingly be doubled, and are 10 : 2.

The equation becomes :

$$2KMnO_4 + 10FeSO_4 + xH_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + xH_2O.$$

The number of sulphate radicals (after making allowance for those supplied by the $FeSO_4$) required in the formation of the molecules of $MnSO_4$, K_2SO_4 and $Fe_2(SO_4)_3$ is estimated by inspection, and this gives $x = 8$.

Reaction III : the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.

$$K_2Cr_2O_7 + KI + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + I_2 + H_2O \text{ (incomplete).}$$

The oxidant $K_2Cr_2O_7$ is reduced to $Cr_2(SO_4)_3$:

$\overset{+2+12-14}{K_2Cr_2O_7} \rightarrow \overset{+6}{Cr_2}(\overset{-6}{SO_4})_3$. The change in O.N. of two atoms of chromium is from +12 to +6, or by 6 units of reduction.

The reductant KI is oxidised to I_2;

$\overset{+1-1}{K\,I} \rightarrow \overset{0}{I_2}$. The change in O.N. of one atom of iodine is from −1 to 0, or by 1 unit of oxidation.

Since 1 molecule of $K_2Cr_2O_7$ undergoes 6 units of reduction and 1 molecule of KI suffers 1 unit of oxidation, the two will react with one another in the ratio of $K_2Cr_2O_7$: 6KI.

The equation will therefore be:

$$K_2Cr_2O_7 + 6KI + xH_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + xH_2O.$$

Inspection shows that x must be 7 in order to account for the number of molecules of $Cr_2(SO_4)_3$ and K_2SO_4 formed.

Reaction IV: the reduction of ferric chloride by hydrogen sulphide.

$$FeCl_3 + H_2S = FeCl_2 + S + H_2O \text{ (incomplete)}.$$

The oxidant $FeCl_3$ is reduced to $FeCl_2$:

$\overset{+3-3}{FeCl_3} \rightarrow \overset{+2\ -2}{FeCl_2}$. The change in O.N. of iron is from +3 to + 2, or by 1 unit of reduction.

The reductant H_2S is oxidised to free S:

$\overset{+2-2}{H_2S} \rightarrow \overset{0}{S}$. The change in O.N. of the sulphur is from −2 to 0, or by 2 units of oxidation.

Two molecules of $FeCl_3$ therefore react with one molecule of H_2S, and this fact, coupled with inspection of the incomplete equation, gives the balanced equation:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

Reaction V: the action of concentrated hydrochloric acid upon potassium permanganate.

$$KMnO_4 + HCl = KCl + MnCl_2 + Cl_2 + H_2O \text{ (incomplete)}.$$

The oxidant $KMnO_4$ is reduced to $MnCl_2$:

$\overset{+1+7-8}{KMnO_4} \rightarrow \overset{+2\ -2}{MnCl_2}$, *i.e.*, the change in O.N. of the manganese is from +7 to +2, or by 5 units of reduction.

The reductant HCl is oxidised to Cl_2:

$\overset{+1-1}{HCl} \rightarrow \overset{0}{Cl_2}$, *i.e.*, the change in O.N. per atom of chlorine is from −1 to 0, or by 1 unit of oxidation.

The $KMnO_4$ and HCl will therefore react in the ratio of 5 : 1. The molecule of chlorine contains two atoms; the number of molecules in the ratio must accordingly be doubled, and are 10 : 2.

The equation becomes:

$$2KMnO_4 + (10 + x)\ HCl = 2KCl + 2MnCl_2 + 5Cl_2 + (5 + x/2)\ H_2O.$$

Inspection shows that x must be 6 in order to account for the formation of the correct number of molecules of KCl and $MnCl_2$ derived from the $KMnO_4$.

I, 25. The Ion-Electron Method.—This method, developed in some detail by Jette and La Mer in 1927, is based upon the conception of oxidation as the loss of one or more electrons, and of reduction as the gain of one or more electrons. The method is limited to ionic reactions in aqueous solutions but, since nearly all the reactions encountered in qualitative analysis are ionic in character, the expression of chemical reactions as interaction between the ions is, for many reasons, an advantage. Furthermore, such ionic reactions can be readily converted into the molecular equations and *vice versa.*

In order to balance an ionic equation by the ion-electron method, the equation is divided into two balanced, partial equations representing the oxidation and reduction respectively. These may be regarded as corresponding to the two half cells described in Sects. **I, 28** and **I, 33** in connexion with the theory of oxidation-reduction. It must be remembered that the reactions take place in aqueous solution so that in addition to the ions supplied by the oxidants and reductants, the molecule of H_2O, H^+ ions and OH^- ions are also present, and may be utilised in balancing the partial ionic equations. The unit change in oxidation or reduction is a change of one electron, which will be denoted by ϵ. To appreciate the principles involved, let us study first the reaction between ferric chloride and stannous chloride in aqueous solution. The partial ionic equation for the reduction is:

$$Fe^{+++} \rightarrow Fe^{++} \qquad (a),$$

and for the oxidation is:

$$Sn^{++} \rightarrow Sn^{++++} \qquad (b).$$

The equations must be balanced not only with regard to the number and kind of atoms but also electrically, that is, the net electric charge on each side must be the same. Equation (*a*) can be balanced by adding one electron to the left hand side:

$$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++} \qquad (a'),$$

and equation (*b*) by adding two electrons to the right hand side:

$$Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon \qquad (b').$$

These partial equations must then be multiplied by coefficients which result in the number of electrons utilised in one reaction being equal to those liberated in the other. Thus equation (*a′*) must be multiplied by two, and we have:

$$2Fe^{+++} + 2\epsilon \rightleftharpoons 2Fe^{++} \qquad (a'');$$

$$Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon \qquad (b'').$$

Adding (*a″*) and (*b″*), we obtain:

$$2Fe^{+++} + Sn^{++} + 2\epsilon \rightleftharpoons 2Fe^{++} + Sn^{++++} + 2\epsilon,$$

and by cancelling the electrons common to both sides, the simple ionic equation is obtained:

$$2\,Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}.$$

The following facts must be borne in mind. All strong electrolytes are completely ionised; hence only the ions actually taking part in or resulting from the reaction need appear in the equation. Substances which are only slightly ionised, such as H_2O, or which are sparingly soluble in water and thus yield only a small concentration of ions, *e.g.*, AgCl and $BaSO_4$, are, in general, written in the molecular form because most of the substance is present in this state.

The complete rules for the application of the ion-electron method may be expressed as follows:—

(1) Ascertain the products of the reaction.

(2) Set up a partial equation for the oxidising agent.

(3) Set up a partial equation for the reducing agent in the same way.

(4) Multiply each partial equation by a factor so that when the two are added the electrons just compensate each other.

(5) Add the partial equations and cancel out substances which appear on both sides of the equation.

A few detailed examples follow.

Reaction I: action of nitric acid upon cadmium sulphide. One partial equation (reduction) is:

$$NO_3^- \rightarrow NO \text{ (incomplete)}.$$

To balance this atomically one must write:

$$NO_3^- + 4H^+ \rightarrow NO + 2H_2O.$$

To balance the latter equation electrically, 3ε must be added to the left hand side:

$$NO_3^- + 4H^+ + 3\epsilon \rightleftharpoons NO + 2H_2O.$$

The second partial equation (oxidation) is:

$$CdS \rightarrow S^\circ.$$

This must be written as :

$$CdS \rightarrow S^\circ + Cd^{++},$$

to balance atomically, and as :

$$CdS \rightleftharpoons S^\circ + Cd^{++} + 2\epsilon,$$

to balance electrically. Thus one nitrate ion requires 3 electrons, and one molecule of cadmium sulphide liberates 2 electrons ; the two partial reactions will take place in the ratio of 2 : 3.

$$\begin{array}{r} 2(NO_3^- + 4H^+ + 3\epsilon = NO + 2H_2O) \\ 3(CdS = S^\circ + Cd^{++} + 2\epsilon) \\ \hline 3CdS + 2NO_3^- + 8H^+ + 6\epsilon = 3Cd^{++} + 3S + 2NO + 4H_2O + 6\epsilon, \\ \textit{or}\ 3CdS + 2NO_3^- + 8H^+ = 3Cd^{++} + 3S + 2NO + 4H_2O. \end{array}$$

Reaction II : the reduction of potassium permanganate by ferrous sulphate in the presence of dilute sulphuric acid.

The first partial equation (reduction) is :

$$MnO_4^- \rightarrow Mn^{++}.$$

To balance this atomically one needs $8H^+$:

$$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O\ ;$$

and to balance it electrically one requires 5ϵ on the left hand side :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O.$$

The second partial equation (oxidation) is :

$$Fe^{++} \rightarrow Fe^{+++}.$$

To balance this electrically one must add one electron to the right hand side (or subtract one electron from the left hand side) :

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon.$$

Now the gain and loss of electrons must be equal. One permanganate ion uses 5 electrons, and one ferrous ion liberates 1 electron ; hence the two partial reactions take place in the ratio of 1 : 5.

$$\begin{array}{r} MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O \\ 5(Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon) \\ \hline \textit{or}\ MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 5Fe^{+++} + 4H_2O. \end{array}$$

Reaction III : the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.

$$Cr_2O_7^{--} \rightarrow Cr^{+++}\ ;$$

$$Cr_2O_7^{--} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O.$$

To balance electrically, add 6ϵ to left hand side:

$$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2\,Cr^{+++} + 7H_2O.$$

The various stages in the deduction of the second partial equation are:

$$\begin{aligned} I^- &\rightarrow I_2\,; \\ 2I^- &\rightarrow I_2\,; \\ 2I^- &\rightleftharpoons I_2 + 2\epsilon. \end{aligned}$$

One dichromate ion uses 6ϵ, and two iodide ions liberate 2ϵ; hence the two partial reactions take place in the ratio of 1 : 3.

$$\begin{array}{r} Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O \\ 3(2I^- \rightleftharpoons I_2 + 2\epsilon) \\ \hline \text{or } Cr_2O_7^{--} + 14H^+ + 6I^- = 2Cr^{+++} + 7H_2O + 3I_2. \end{array}$$

Reaction IV: the reduction of ferric chloride by hydrogen sulphide.

$$\begin{aligned} Fe^{+++} &\rightarrow Fe^{++}\,; \\ Fe^{+++} + \epsilon &\rightleftharpoons Fe^{++}. \\ H_2S &\rightarrow S^\circ\,; \\ H_2S &\rightarrow S^\circ + 2H^+\,; \\ H_2S &\rightleftharpoons S^\circ + 2H^+ + 2\epsilon. \end{aligned}$$

Thus one ferric ion liberates 1 electron, and one molecule of hydrogen sulphide uses 2 electrons. The partial reactions will therefore take place in the ratio of 2 : 1.

$$\begin{array}{r} 2(Fe^{+++} + \epsilon) \rightleftharpoons Fe^{++} \\ H_2S \rightleftharpoons S^\circ + 2H^+ + 2\epsilon \\ \hline 2Fe^{+++} + H_2S = 2Fe^{++} + S + 2H^+. \end{array}$$

Reaction V: the action of concentrated hydrochloric acid upon potassium permanganate.

$$\begin{aligned} MnO_4^- &\rightarrow Mn^{++}\,; \\ MnO_4^- + 8H^+ &\rightarrow Mn^{++} + 4H_2O\,; \\ MnO_4^- + 8H^+ + 5\epsilon &\rightleftharpoons Mn^{++} + 4H_2O. \\ Cl^- &\rightarrow Cl_2\,; \\ 2Cl^- &\rightarrow Cl_2\,; \\ 2Cl^- &\rightleftharpoons Cl_2 + 2\epsilon. \end{aligned}$$

One permanganate ion utilises 5ϵ, and two chloride ions liberate 2ϵ, hence the two partial reactions take place in the ratio of 2 : 5.

$$
\begin{array}{r}
2(MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O) \\
5(2Cl^- \rightleftharpoons Cl_2 + 2\epsilon) \\
\hline
2MnO_4^- + 16H^+ + 10Cl^- = 2Mn^{++} + 5Cl_2 + 8H_2O.
\end{array}
$$

The student should experience little difficulty in balancing the common equations by the ion-electron method and converting them into molecular equations. A brief resumé will now be given of a few typical oxidising and reducing agents and the reactions which they undergo. This will be useful for reference purposes. The reader should attempt to deduce the ionic equations independently, and also to formulate the corresponding molecular equations.

I, 26. TYPICAL OXIDISING AND REDUCING AGENTS : SUMMARY

Oxidising Agents.—*Potassium permanganate.* Its action depends upon the conversion of the manganese into a manganese compound with a lower valency or with a lower oxidation number. In acid solution, the oxidation number of manganese changes from +7 to +2, or by 5 units of reduction. Expressed ionically, MnO_4^- is converted into Mn^{++} ; this involves a gain of 5 electrons.

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O$$

Some of the ionic reactions which potassium permanganate undergoes, are :

$$
\begin{array}{llllll}
MnO_4^- + 5Fe^{++} & + \; 8H^+ & = Mn^{++} & + 5Fe^{+++} & + 4H_2O. \\
2MnO_4^- + 10I^- & + \; 16H^+ & = 2Mn^{++} & + 5I_2 & + 8H_2O. \\
2MnO_4^- + 5H_2S & + \; 6H^+ & = 2Mn^{++} & + 5S & + 8H_2O.
\end{array}
$$

In neutral or alkaline solution, the manganese in the permanganate is generally reduced to MnO_2, *i.e.*, by 3 units of reduction. Ionically expressed, the change of MnO_4^- into MnO_2 corresponds to a gain of 3 electrons. An example of this is the oxidation of manganese salts to MnO_2, to which it is itself reduced.

$$* \; 2MnO_4^- + 3Mn^{++} + 2H_2O = 5MnO_2 + 4H^+.$$

Potassium dichromate. Its action depends upon the conversion of the chromium into a chromic compound. In acid solution, the O.N. of two atoms of chromium changes from +12 to +6, or by 6 units of reduction. Ionically expressed, $Cr_2O_7^{--}$ is converted into $2Cr^{+++}$, and this corresponds to a gain of 3 electrons per atom of chromium.

$$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O.$$

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ = 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

$$Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 3I_2 + 7H_2O.$$

$$Cr_2O_7^{--} + 3Sn^{++} + 14H^+ = 2Cr^{+++} + 3Sn^{++++} + 7H_2O.$$

$$Cr_2O_7^{--} + \underset{\text{(formaldehyde)}}{3H.CHO} + 8H^+ = 2Cr^{+++} + \underset{\text{(formic acid)}}{3H.COOH} + 4H_2O.$$

Nitric Acid. The oxidising action is dependent upon the reduction of the nitrogen. The nature of the reduction varies with the concentration of the acid and with the compound to be oxidised. The most common product is nitric oxide, but nitrogen dioxide, nitrous oxide, nitrogen and ammonia are also formed under different experimental conditions.

In the conversion of the nitrogen in nitric acid into nitric oxide, the O.N. changes from +5 to +2, or by 3 units of reduction. Expressed ionically, the transformation of NO_3^- into NO results in a gain of 3 electrons.

$$NO_3^- + 2H^+ + \epsilon \rightleftharpoons NO_2 + H_2O.$$

$$NO_3^- + 4H^+ + 3\epsilon \rightleftharpoons NO + 2H_2O.$$

$$3CuS + 2NO_3^- + 8H^+ = 3Cu^{++} + 3S + 2NO + 4H_2O.$$

$$3Fe^{++} + NO_3^- + 4H^+ = 3Fe^{+++} + NO + 2H_2O.$$

$$3Ag + NO_3^- + 4H^+ = 3Ag^+ + NO + 2H_2O.$$

The halogens. Here the action is dependent upon the conversion of the neutral and free halogen into halogen ions by accepting electrons.

$$Cl_2 + 2\epsilon \quad 2Cl^-$$

$$2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-.$$

The oxidising action of *aqua regia* may be ascribed to the free chlorine which is liberated in the reaction :

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Hydrogen peroxide. This substance acts as both an oxidising and reducing agent. The former action, particularly in acid solution, is usually attributed to the presence of one atom of oxygen differing in its mode of attachment from the other oxygen atom.

$$2Fe^{++} + H_2O_2 + 2H^+ = 2Fe^{+++} + 2H_2O.$$

Reducing Agents.—*Sulphur dioxide or sulphurous acid.* The reducing action is dependent upon the conversion of the sulphite ion into the sulphate ion. Often the reagent is employed by adding sodium sulphite to the slightly acidified solution to be reduced. The O.N. of the sulphur changes from +4 to +6, or by two units of oxidation. Expressed ionically, the SO_3^{--} ion passes into the SO_4^{--} ion, and this corresponds to a loss of 2 electrons per atom of sulphur.

$$SO_3^{--} + H_2O = SO_4^{--} + 2H^+ + 2\epsilon.$$

$$SO_3^{--} + 2Fe^{+++} + H_2O = SO_4^{--} + 2Fe^{++} + 2H^+.$$

$$SO_3^{--} + I_2 + H_2O = SO_4^{--} + 2I^- + 2H^+.$$

$$3SO_3^{--} + 2CrO_4^{--} + 10H^+ = 3SO_4^{--} + 2Cr^{+++} + 5H_2O.$$

$$SO_3^{--} + AsO_4^{---} = SO_4^{--} + AsO_3^{---}.$$

Hydrogen sulphide. The action depends upon the conversion of the sulphur with an O.N. of −2 into free sulphur with an O.N. of zero, *i.e.*, by 2 units of oxidation. Expressed ionically, the change involves the loss of 2 electrons per molecule of hydrogen sulphide.

$$S^{--} \rightleftharpoons S^\circ + 2\epsilon.$$

$$3H_2S + Cr_2O_7^{--} + 8H^+ = 3S + 2Cr^{+++} + 7H_2O.$$

$$5H_2S + 2MnO_4^- + 6H^+ = 5S + 2Mn^{++} + 8H_2O.$$

$$H_2S + 2Fe^{+++} = S + 2Fe^{++} + 2H^+.$$

$$H_2S + Cl_2 = S + 2H^+ + 2Cl^-.$$

$$3H_2S + 2NO_3^- + 2H^+ = 3S + 2NO + 4H_2O.$$

Hydriodic acid. Here the iodine ion passes into free iodine; the O.N. changes from −1 to 0, or by 1 unit of oxidation. This is equivalent to the loss of 1 electron.

$$2I^- \rightleftharpoons I_2 + 2\epsilon.$$

$$2I^- + 2Fe^{+++} = I_2 + 2Fe^{++}.$$

$$6I^- + Cr_2O_7^{--} + 14H^+ = 3I_2 + 2Cr^{+++} + 7H_2O.$$

$$10I^- + 2MnO_4^- + 16H^+ = 5I_2 + 2Mn^{++} + 8H_2O.$$

Stannous chloride. The reducing action, which usually occurs in acid solution, is dependent upon the facile conversion of stannous ions into stannic ions; the change in O.N. is from +2 to +4, or by 2 units of oxidation. This is equivalent to the loss of 2 electrons.

$$Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon.$$

$$Sn^{++} + 2HgCl_2 = Sn^{++++} + Hg_2Cl_2 + 2Cl^-.$$

$$Sn^{++} + Hg_2Cl_2 = Sn^{++++} + 2Hg + 2Cl^-.$$

$$Sn^{++} + Cl_2 = Sn^{++++} + 2Cl^-.$$

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}.$$

Metals and hydrogen. The use of metals and of hydrogen as reductants is based upon the conversion of the metal and of neutral hydrogen into cations. The change requires an increase in O.N., or a loss of electrons, dependent upon the valency of the metal. With hydrogen, the increase in O.N. is 1 for each atom, and this corresponds to a loss of 1 electron. The reduction may take place in neutral, acid or alkaline solution.

$$Zn \rightleftharpoons Zn^{++} + 2\epsilon.$$

$$4Zn + NO_3^- + 7OH^- = 4ZnO_2^{--} + NH_3 + H_2O.$$

$$2Al + 2OH^- + 2H_2O = 2AlO_2^- + 3H_2.$$

$$Fe + 2H^+ = Fe^{++} + H_2.$$

$$Zn + 2Fe^{+++} = Zn^{++} + 2Fe^{++}.$$

A useful summary of the common oxidising and reducing agents, together with the various transformations which they undergo, is given in Table X.

TABLE X.

COMMON OXIDISING AGENTS.

Substance	*Radical or element involved*	*O.N. of "effective" element*	*Reduction product*	*New O.N.*	*Decrease in O.N.*	*Gain in electrons*
$KMnO_4$ (acid)	MnO_4^-	+ 7	Mn^{++}	+2	5	5
$KMnO_4$ (alkaline)	MnO_4^-	+ 7	MnO_2 (or Mn^{++++})	+4	3	3
$K_2Cr_2O_7$	$Cr_2O_7^{--}$	+6	Cr^{+++}	+3	3	3
HNO_3 (dil.)	NO_3^-	+5	NO	+2	3	3
HNO_3 (conc.)	NO_3^-	+5	NO_2	+4	1	1
Cl_2	Cl	0	Cl^-	−1	1	1
Br_2	Br	0	Br^-	−1	1	1
I_2	I	0	I^-	−1	1	1
3HCl : 1HNO_3	Cl	0	Cl^-	−1	1	1
H_2O_2	O	0	O^{--}	−2	2	2
Na_2O_2	O	0	O^{--}	−2	2	2
$KClO_3$	ClO_3^-	+5	Cl^-	−1	6	6
$KBrO_3$	BrO_3^-	+5	Br^-	−1	6	6
KIO_3	IO_3^-	+5	I^-	−1	6	6
NaOCl	OCl^-	+1	Cl^-	−1	2	2

The *equivalent weight of a normal salt* is that weight of it which contains one gram equivalent weight of the cation or anion. This quantity will be the molecular weight of the salt divided by the total valency of the cation or anion. Thus the equivalent weight of KCl is 1 mol, of Na_2SO_4 1/2 mol, of $AlCl_3$ 1/3 mol, of $SnCl_4$ 1/4 mol and of $Ca_3(PO_4)_2$ 1/6 mol.

For *acid and double salts,* the equivalent weight may vary with the component to which the equivalent is referred. Thus for the salt $Na_2HAsO_4,12H_2O$, which yields the ions $2Na^+$, $HAsO_4^{--}$, H^+ and AsO_4^{---} upon progressive ionisation the equivalent will be 1/2 mol when referred to Na^+ or $HAsO_4^{--}$, 1 mol when referred to H^+, and 1/3 mol when referred to AsO_4^{---}. With a double salt, like chrome alum $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, the equivalent weight will be 1/2, 1/6 and 1/8 mol respectively according as to whether the reacting component is K^+, Cr^{+++} or SO_4^{--}. It must clearly be pointed out that the above remarks apply only to the calculation of the equivalents of salts which do not function as oxidising or reducing agents. The *equivalent weight of a salt,* which does not act as an oxidant or reductant, is the gram molecular weight divided by the total valency of the reacting constituent.

The *equivalent weight of an oxidising agent* is determined by the *change in oxidation number** which the reduced element experiences. It is that quantity of oxidant which involves a change of one unit in the oxidation number.† Thus in the normal reduction of potassium permanganate in the presence of dilute sulphuric acid to a manganous salt,

$$\overset{+1+7-8}{KMnO_4} \rightarrow \overset{+2+6-8}{MnSO_4},$$

the change in oxidation number of the manganese is from +7 to +2, or by 5 units of reduction. The equivalent weight is therefore 1/5 mol (compare Sects. **I, 24** and **I, 26**). Similarly for the reduction of potassium dichromate in acid solution,

$$\overset{+2+12-14}{K_2Cr_2O_7} \rightarrow \overset{+6\quad-6}{Cr_2(SO_4)_3},$$

---

* Treadwell and Hall, in their *Quantitative Analysis*, call this polarity. The present author prefers the term oxidation number, first employed by McAlpine and Soule in their treatise *Qualitative Chemical Analysis*, owing to the confusing ideas that "polarity" might summon to the mind of the reader.

† The standard of reference may be taken as the reaction:

$$H^\circ \rightleftharpoons H^+ + \epsilon, \text{ or } 1/2\ H_2 \rightleftharpoons H^+ + \epsilon.$$

This involves unit change in oxidation number. Incidentally this equation clearly shows the relation between the oxidation number method and the ion-electron method for deducing equivalent weights.

the change in O.N. of two atoms of chromium is from +12 to +6, or by 6 units of reduction. The equivalent weight of $K_2Cr_2O_7$ is accordingly 1/6 mol. In order to find the equivalent weight of an oxidising agent, one divides the molecular weight by the total change in O.N. *per molecule* which some element in the substance undergoes.

We may also employ the ion-electron method (Sect. **I, 25**). The partial ionic equation in which the oxidising agent takes part is first written down. For potassium permanganate in acid solution, this is :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O.$$

The equivalent weight of an oxidising agent in a particular reaction is then that weight of the oxidant which is associated with a gain of one electron in that reaction. In the example under consideration 5 electrons are gained, hence the equivalent weight is 1/5 mol. In general, to calculate the equivalent weight of an oxidising agent for a particular reaction, one divides the gram molecular weight by the number of electrons per molecule indicated in the partial ionic equation as taking part in the reaction.

The *equivalent weight of a reducing agent* is similarly determined by the change in oxidation number which the oxidised element suffers. Consider the conversion of ferrous into ferric sulphate :

$$2(\overset{+2}{Fe}\overset{-2}{SO_4}) \rightarrow \overset{+6}{Fe_2}\overset{-6}{(SO_4)_3}.$$

Here the change in O.N. per *atom* of iron is from +2 to +3, or by 1 unit of oxidation, hence the equivalent weight of ferrous sulphate is 1 mol. The ion-electron method may also be employed ; the procedure is exactly analogous to that described under oxidising agents. One example will be studied, *viz.*, the conversion of sodium sulphite into sodium sulphate. The partial ionic equation is :

$$SO_3^{--} + H_2O - 2\epsilon \rightleftharpoons SO_4^{--} + 2H^+.$$

Two electrons are lost per gram molecular weight of sodium sulphite ; the equivalent weight is accordingly 1/2 mol.

In general, it may be stated : (i) The equivalent weight of an element taking part in an oxidation-reduction (redox) reaction is the atomic weight divided by the change in oxidation number. (ii) When an atom in any complex molecule suffers a change in oxidation number (oxidation or reduction), the equivalent weight of the molecule is the molecular weight divided by the change in oxidation number of the oxidised or reduced element. If more than one atom of the reactive element is present, the molecular weight is divided by the total change in O.N.

For convenience of reference the partial ionic equations for a number of oxidising and reducing agents are collected in Table XI (compare Table X).

TABLE XI.—IONIC EQUATIONS FOR USE IN THE CALCULATION OF THE EQUIVALENT WEIGHTS OF OXIDISING AND REDUCING AGENTS.

Substance	*Partial Ionic Equation*
	OXIDANTS
Potassium permanganate (acid)	$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O$
Potassium permanganate (neutral)	$MnO_4^- + 2H_2O + 3\epsilon \rightleftharpoons MnO_2 + 4OH^-$
Potassium dichromate	$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O$
Ceric sulphate	$Ce^{++++} + \epsilon \rightleftharpoons Ce^{+++}$
Chlorine	$Cl_2 + 2\epsilon \rightleftharpoons 2Cl^-$
Ferric chloride	$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$
Potassium iodate	$IO_3^- + 6H^+ + 6\epsilon \rightleftharpoons I^- + 3H_2O$
Sodium hypochlorite	$ClO^- + H_2O + 2\epsilon \rightleftharpoons Cl^- + 2OH^-$
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2\epsilon \rightleftharpoons 2H_2O$
Manganese dioxide	$MnO_2 + 4H^+ + 2\epsilon \rightleftharpoons Mn^{++} + 2H_2O$
Sodium bismuthate	$BiO_3^- + 6H^+ + 2\epsilon \rightleftharpoons Bi^{+++} + 3H_2O$
Nitric acid (conc.)	$NO_3^- + 2H^+ + \epsilon \rightleftharpoons NO_2 + H_2O$
Nitric acid (dil.)	$NO_3^- + 4H^+ + 3\epsilon \rightleftharpoons NO + 2H_2O$
	REDUCTANTS
Hydrogen	$H_2 - 2\epsilon \rightleftharpoons 2H^+$
Zinc	$Zn - 2\epsilon \rightleftharpoons Zn^{++}$
Hydrogen sulphide	$H_2S - 2\epsilon \rightleftharpoons 2H^+ + S$
Hydrogen iodide	$2HI - 2\epsilon \rightleftharpoons I_2 + 2H^+$
Oxalic acid	$C_2O_4^{--} - 2\epsilon \rightleftharpoons 2CO_2$
Ferrous sulphate	$Fe^{++} - \epsilon \rightleftharpoons Fe^{+++}$
Sulphurous acid	$H_2SO_3 + H_2O - 2\epsilon \rightleftharpoons SO_4^{--} + 4H^+$
Stannous chloride	$Sn^{++} - 2\epsilon \rightleftharpoons Sn^{++++}$
Stannous chloride (in presence of hydrochloric acid)	$Sn^{++} + 6Cl^- - 2\epsilon \rightleftharpoons SnCl_6^{--}$
Hydrogen peroxide	$H_2O_2 - 2\epsilon \rightleftharpoons 2H^+ + O_2$
Sodium thiosulphate	$2S_2O_3^{--} - 2\epsilon \rightleftharpoons S_4O_6^{--}$

We are now in a position to understand more clearly why the equivalent weights of substances vary with the reaction. A normal solution of ferrous sulphate $FeSO_4,7H_2O$ will have an equivalent weight of 1 mol when employed as a reducing agent and 1/2 mol when employed as a normal salt or precipitant. A solution of ferrous sulphate which is normal as a salt, will be $N/2$ as a reducing agent. A few other examples are collected below.

Oxalic Acid. $H_2C_2O_4,2H_2O$. This compound contains two replaceable hydrogen atoms, hence a normal solution contains 1/2 mol per litre.

$$2H^+ + 2OH^- = 2H_2O,$$

or

$$H_2C_2O_4 + 2KOH = K_2C_2O_4 + 2H_2O.$$

As a reducing agent, the partial ionic equation is :

$$C_2O_4^{--} - 2\epsilon \rightleftharpoons 2CO_2,$$

so that the equivalent weight is 1/2 mol.

Potassium hydrogen oxalate. KHC_2O_4. This substance has one replaceable hydrogen atom, hence, as an acid, the equivalent is 1 mol :

$$KHC_2O_4 + KOH = K_2C_2O_4 + H_2O.$$

When functioning as a reducing agent, the reducing power is due to the $C_2O_4^{--}$, and the equivalent is 1/2 mol.

Potassium tetroxalate. $KHC_2O_4,H_2C_2O_4,2H_2O$. This salt contains three replaceable hydrogen atoms, and its equivalent weight is therefore 1/3 mol.

$$KHC_2O_4,H_2C_2O_4,2H_2O + 3KOH = 2K_2C_2O_4 + 5H_2O.$$

As a reducing agent, a gram molecular weight contains $2C_2O_4^{--}$ and the equivalent weight is therefore 1/4 mol. A solution of this salt which is $3N$ as an acid is $4N$ as a reducing agent.

Potassium permanganate. $KMnO_4$. As a salt, that is, as a precipitant, the equivalent weight is 1 mol. We have already seen (Section **26** ; Tables X and XI) that the equivalent weight in acid solution is 1/5 mol, and in neutral or alkaline solution 1/3 mol. A solution of $KMnO_4$ which is $0{\cdot}1N$ as a precipitant, is $0{\cdot}5N$ as an oxidising agent in acid solution, and $0{\cdot}3N$ as an oxidising agent in neutral or alkaline solution.

Once the reader has grasped the above concepts as to the calculation of equivalent weights, he should experience no difficulty in computing the exact amount of substance required in the preparation of any solution required in qualitative analysis. The strengths of the reagents employed, together with details for their preparation, are collected in the Appendix (Section **A, 2**).

I, 28. THEORY OF OXIDATION AND REDUCTION

Reference has already been made in Sect. **I, 23** to the fact that oxidation consists of the loss of electrons and reduction of the gain of electrons. Thus in the reduction of ferric chloride by stannous chloride :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

or $$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++},$$

for every atomic weight (56 grams) of iron reduced 96,500 coulombs or 1 Faraday of electricity is lost by the iron, and for every atomic weight (119 grams) of tin oxidised, the latter has gained 2 × 96,500 coulombs or 2 Faradays.*

According to modern theory, an electric current consists in the transfer of electrons. It should therefore be possible to obtain direct proof of the transfer of electricity in the oxidation-reduction reaction under suitable experimental conditions. This is clearly shown by the following experiment (Fig. 2). Solutions of stannous chloride and of ferric chloride, each acidified with dilute hydrochloric acid to increase the conductivity, are placed in separate beakers A and B, and the two solutions are connected by means of a " salt bridge " containing sodium chloride. The latter consists of an inverted U-tube filled with a solution of a conducting electrolyte, such as sodium chloride, and stoppered at each end with a plug of cotton wool to arrest mechanical flow. It connects the two parts of the redox system preventing mixing. The electrolyte in solution in the salt bridge is always selected so that it does not react chemically with either of the solutions which it connects. Platinum foil electrodes are introduced into each of the solutions, and the two electrodes are connected to a millivoltmeter V. When the circuit is closed, it will be found that the current in the

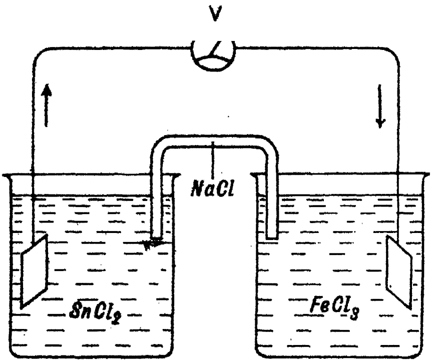

Fig. 2

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* It follows from Faraday's law that each gram equivalent weight of an ion is associated with a charge of one Faraday of electricity. A change of charge of one thus corresponds to the gain or loss of one Faraday per formula weight of the substance.

external circuit passes from the stannous chloride solution to the ferric chloride solution. After a little time, stannic ions can be detected in A and ferrous ions in B.

In the preceding experiment the flow of current is due to the e.m.f. produced by the chemical change in the redox reaction. It can also be shown that an electric current, say from a storage battery, will give rise to oxidation-reduction reactions. Thus if in Fig. 2 beaker A contains ferrous ammonium sulphate acidified with dilute sulphuric acid, and beaker B ferric chloride likewise acidified with dilute sulphuric acid, the salt bridge dilute sulphuric acid, and the millivoltmeter be replaced by a 6-volt battery, then after some time ferric ions can be detected with potassium thiocyanate solution in A and ferrous ions with potassium ferricyanide solution in B.

It is a well-known fact that oxidants and reductants vary considerably in strength. Information of a qualitative nature as to the relative strengths (compare relative strengths of weak acids and bases as expressed by their dissociation constants in Table VI) would be of considerable practical value. A method which suggests itself at once is the measurement of the e.m.f. of redox reactions under standard conditions. This is indeed the method which is employed, but before this can be understood by the student, it will be necessary to consider the subject of electrode potentials.

I, 29. Electrode potentials.—The vapour pressure of a liquid or solid is a measure of its tendency to pass into the gaseous state. If excess of a non-electrolyte, like sugar, is placed in contact with water, it will pass into solution until equilibrium is obtained, that is, until the concentration of the sugar in the solution is equal to the solubility (saturated solution). Owing to the analogy between dissolved substances and gases, the tendency of a substance to enter into solution is known as the *solution pressure.* There will clearly be some force which acts in opposition to the solution pressure, otherwise unlimited quantities would pass into solution ; this force is the osmotic pressure which the molecules of the dissolved substance exert in solution. At equilibrium, *i.e.*, in a saturated solution, the solution pressure of the substance is exactly balanced by the osmotic pressure. This reasoning also applies if the substance is an electrolyte.

When a metal is immersed in a solvent such as water, there will be a tendency for ions of the metals to pass into solution.

Nernst termed this tendency the *electrolytic solution pressure* (P) of the metal. If a metal is immersed in a solution of one of its salts, the tendency of the metal to pass into solution in the form of its ions will be opposed by the osmotic pressure of the ions p; the latter will tend to deposit the metal ions upon the metal. When, say, zinc is placed in contact with zinc sulphate solution, some zinc ions pass into solution by virtue of the electrolytic solution pressure of the metal and thus the zinc is left with a negative charge; a potential difference therefore exists between the metal and the solution. Owing to the comparatively large charge which the ions carry, they do not move far away from the metal, but are held by electrostatic attraction and form an " electrical double layer." The attraction of the opposite charges prevents the further formation of ions from the metal, and an equilibrium with a definite potential difference is rapidly attained when only a minute amount of the zinc has passed into the ionic state. The greater the concentration of the ions in solution, the greater will be the tendency of these ions to give up their charge to the metal. The potential difference established between a metal and the solution, or the *electrode potential*, will therefore be dependent upon the concentration (and consequently upon the osmotic pressure) of the ions of the metal in the solution. For zinc, P is so great that the metal forms ions in most solutions of its salts, and therefore becomes negatively charged relatively to the solution. For copper, P is comparatively small and, in general, the ions have so great a tendency to deposit their charge upon the metal that the latter is usually positively charged when placed in a solution of a copper salt.

The metals zinc and copper are examples of two general cases which arise.

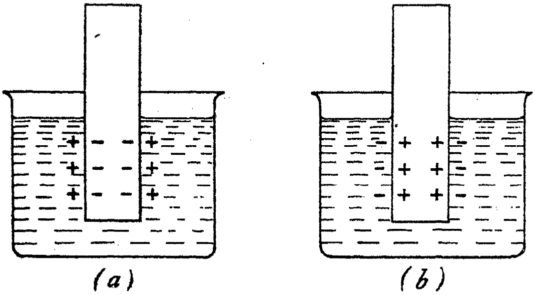
(a) (b)

Fig. 3

Case 1. The electrolytic solution pressure of the metal is greater than the osmotic pressure of the ions of the metal, *i.e.*, $P > p$. Here positive ions will pass into solution. As a result the metal will be left with a negative charge, the solution bathing it will be positively charged (Fig. 3, (*a*)), and a difference of potential is established between the metal and the solution.

Examples of such elements are cadmium, zinc, manganese and the alkali metals.

Case 2. The electrolytic solution pressure of the metal is less than the osmotic pressure of the ions, *i.e.*, $p > P$. In this case positive ions will be deposited on the surface of the metal. This results in the metal acquiring a positive charge, the solution immediately surrounding it a negative charge (Fig. 3 (*b*)), and the establishment of a potential difference between the metal and the solution.

Examples of such metals with low solution pressures are silver, copper, mercury, gold and platinum. In some cases the ionic concentration may be so far reduced that $p < P$, the sign of the electrode potential is then reversed.

A third case in which $P = p$ is theoretically possible. In this system the tendency for ions from the metal to pass into solution is exactly balanced by their tendency to leave the solution and deposit upon the metal. No " electrical double layer " is accordingly formed, and hence no potential difference exists between the metal and the solution.

Summarising the above discussion, it may be stated that when a metal and a solution are not initially in equilibrium, an " electrical double layer," consisting of the charge on the surface of the metal and an equal charge of opposite sign facing it in the solution, is formed, and as a consequence of the latter there is a difference of potential between the metal and the solution. The potential difference is measured by the amount of work done in transferring unit positive charge from a point in the interior of the liquid to a point inside the metal.

The above theory of the origin of the e.m.f. is due to Nernst (1889). Recently other theories have been proposed by Butler (1924) and by Gurney and Fowler (1932) (for an account of these the reader is referred to Butler, *Chemical Thermodynamics*, 1935, p. 129 ; Dole, *Electrochemistry*, 1935, p. 505), but these are beyond the scope of this book. Nernst deduced the following expression for computing the potential difference which exists between a metal and a solution of its ions, that is, for the electrode potential E:

$$E = \frac{RT}{nF} \log_e \frac{p}{P},$$

where R is the gas constant expressed in electrical units, F is the quantity of electricity borne by one equivalent weight in grams (one Faraday), n the valency of the ions and T the absolute temperature. The expression reduces to:

$$E_{18^\circ} = \frac{0{\cdot}0577}{n} \log \frac{p}{P} \text{ volts, and } E_{25^\circ} = \frac{0{\cdot}0591}{n} \log \frac{p}{P} \text{ volts}$$

at 18°C and 25°C respectively. The osmotic pressure p is directly proportional to the concentration of the solution and to the absolute temperature, the e.m.f. will therefore vary with the concentration. If the concentration is increased tenfold, the e.m.f. increases by 0·06 volt for a univalent ion, by $0{\cdot}06/2 = 0{\cdot}03$ volt for a bivalent ion, *etc.* The electrolytic solution pressure provides a measure of the tendency of the metal to be converted into ions or, since the formation of ions constitutes an oxidation, it is also a measure of the capacity of the metal to undergo oxidation.

In order to determine the potential difference between an electrode and a solution, it is necessary to have another electrode and a solution, the potential difference between which is known. These two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be directly measured. The e.m.f. of the cell is the arithmetical sum or difference of the two electrode potentials (depending upon the sign of these two potentials); the value of the unknown potential can then be calculated. In practice the standard electrode potential used for comparative purposes is the *molar hydrogen electrode.* This consists of a piece of platinum foil, coated with platinum black by an electrolytic process, and immersed in a solution of hydrochloric acid, molar with respect to hydrogen ions (more correctly in a solution of hydrochloric acid containing hydrogen ions of unit activity). Hydrogen gas at a pressure of one atmosphere is passed over the foil through the side tube C (Fig. 4) and escapes through the small openings B in the surrounding glass tube A; the foil is thus kept saturated with the gas. Connection between the platinum foil sealed into the tube D with an outer circuit is made with mercury in D. The platinum black has the remarkable property of adsorbing large quantities of hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode. Under fixed conditions, *viz.*, of atmospheric pressure and molar concentration of hydrogen ions in the solution in contact with the electrode, the hydrogen electrode possesses a definite potential at all temperatures. By connecting the molar hydrogen electrode with a metal electrode (a metal in contact with a molar solution of its ions) by means of a salt (say potassium chloride) bridge, the *molar* or *standard electrode potential* may be directly determined. Other electrodes, particularly the calomel electrode and the silver—silver chloride electrode, the potentials of which have been determined by direct reference to the molar hydrogen electrode, are often used in practice owing to convenience of manipulation. The former is referred to again in Section **I, 38.** but for a fuller treatment the student is referred to text-books of electrochemistry.*

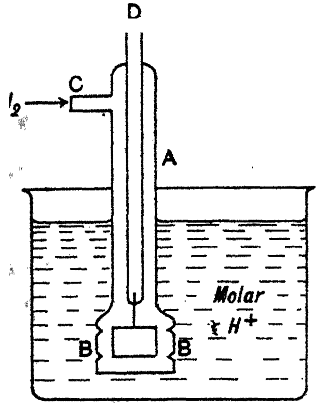

Fig. 4

When a rod of zinc is immersed in a molar solution of zinc ions and this is coupled with a molar hydrogen electrode, the resultant cell :

$$\mathrm{Zn} \mid \mathrm{Zn}^{++}\,(M) \parallel \mathrm{H}^{+}(M) \mid \mathrm{H}_2,\ \mathrm{Pt},$$

has an e.m.f. of 0·76 volt. The two reactions which take place are :

$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{++} + 2\epsilon, \text{ and } \mathrm{H}_2 + 2\epsilon \rightleftharpoons 2\mathrm{H}^{+}.$$

The zinc pole is negative and therefore the zinc electrode is 0·76 volt more negative than the hydrogen electrode, or the potential of the molar zinc electrode is − 0·76 volt (the molar hydrogen electrode is arbitrarily taken as equal to zero). Further, if one employs a copper electrode immersed in a molar solution of cupric ions, and couples this with a molar hydrogen electrode, the cell has an e.m.f. of 0·34 volt. The copper pole is now positive ; the potential of the molar copper electrode is accordingly + 0·34 volt.

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*See for example, Glasstone, *The Electochemistry of Solutions* (1937).

The *standard* or *molar electrode potential* of an element may therefore be defined as the e.m.f. produced when a half cell consisting of the element immersed in a molar solution of its ions (more correctly in a solution of its ions possessing unit activity) is coupled with a molar hydrogen electrode, the potential of which is assumed equal to zero. Table XII gives a list of standard electrode potentials at 25°*C*; the sign of the potential here adopted is that of the charge on the electrode.

TABLE XII. STANDARD ELECTRODE POTENTIALS AT 25°*C*

Li/Li^+	−2·959	Ni/Ni^{++}	−0·231
K/K^+	−2·924	Sn/Sn^{++}	−0·136
Na/Na^+	−2·715	Pb/Pb^{++}	−0·122
Mg/Mg^{++}	−1·55	$Pt(H_2)/H^+$	0·000
Al/Al^{+++}	−1·33	Cu/Cu^{++}	+0·344
Zn/Zn^{++}	−0·762	Hg/Hg^{++}	+0·799
Fe/Fe^{++}	−0·441	Ag/Ag^+	+0·798
Cd/Cd^{++}	−0·401	Pd/Pd^{++}	+0·82
Co/Co^{++}	−0·29	Au/Au^{+++}	+1·36

When metals are arranged in the order of their standard electrode potentials, the so-called *electrochemical series* of the metals is obtained. The greater the negative value of the potential, the greater is the tendency of the metal to pass into the ionic state. A metal with a more negative potential will displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminium, zinc or iron will displace copper from solutions of its salts; lead will displace copper, mercury or silver; copper will displace silver or mercury.

The standard electrode potential is a quantitative expression of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent; the more negative the element, the more powerful its action as a reductant.

I, 30. Calculation of electrode potentials.—The Nernst equation:

$$E = \frac{RT}{nF} \log_e \frac{p}{P}$$

may be written in the form:

$$E = \frac{RT}{nF} \log_e p \quad \frac{RT}{nF} \log_e P.$$

At constant temperature the term $\frac{RT}{nF}\log_e P$ is a constant for a given metal ; hence :

$$E = \frac{RT}{nF}\log_e p + \text{constant.}$$

The gas laws may be written in the form $p = RTc$, where c is the concentration of the positive ions in the solution. More accurately, the expression should be $p = \mathrm{RT}a_+$ where a_+ is the activity of the ions.

$$\text{Thus } E = \frac{RT}{nF}\log_e a_+ + \text{constant } (E_0).$$

The equation can be simplified by substituting the known values of the constants and converting the logarithms to base 10 ; it then becomes :

$$E = \frac{0{\cdot}0001982\ T}{n}\log a_+ + \mathrm{E}_0.$$

For a temperature of 25°C (T = 288°) :

$$E = \frac{0{\cdot}0591}{n}\log a_+ + E_\circ \qquad \text{(i).}$$

Before the introduction of the activity concept, the concentration of the ions c_{i+} (in mols per litre) was used in place of the activity :

$$E = \frac{0{\cdot}0591}{n}\log c_{i+} + E_\circ \qquad \text{(i').}$$

The latter expression is sufficiently accurate for most practical purposes in qualitative analysis.

For a non-metal, which yields negative ions, equation (i) becomes

$$E = E_\circ - \frac{0{:}0591}{n}\log a_-,$$

where a_- is the activity of the negative ions. For purposes of calculation $c_{i\_}$ may replace a_-.

It will be seen that for a solution of unit activity, where a_+ or a_- is unity, $E = E_\circ$: thus $E_\circ$ is the *standard* or *molar electrode potential* of the element. Knowing the value of $E_\circ$, the potential for any concentration can be calculated with the aid of equation (i').

An interesting application of this equation is to the calculation of equilibrium constants.

Example 8. Calculate the equilibrium constant of the reaction :

$$Zn^\circ + Cu^{++} \rightleftharpoons Zn^{++} + Cu^\circ.$$

This is the familiar displacement of cupric ions from solutions by metallic zinc.

For the zinc electrode :

$$E_{Zn} = E_\circ + \frac{0{\cdot}059}{2} \log [Zn^{++}],$$

$$= -0{\cdot}76 + 0{\cdot}0295 \log [Zn^{++}].$$

For the copper electrode :

$$E_{Cu} = E_\circ + \frac{0{\cdot}059}{2} \log [Cu^{++}],$$

$$= +\,0{\cdot}34 + 0{\cdot}0295 \log [Cu^{++}].$$

At equilibrium $E_{Zn} = E_{Cu}$.

$$-\,0{\cdot}76 + 0{\cdot}0295 \log [Zn^{++}] = +\,0{\cdot}34 + 0{\cdot}0295 \log [Cu^{++}],$$

$$\textit{or} \qquad \log \frac{[Zn^{++}]}{[Cu^{++}]} = \frac{1{\cdot}10}{0{\cdot}0295} = 37{\cdot}3,$$

$$\textit{or} \qquad \frac{[Zn^{++}]}{[Cu^{++}]} = 2 \times 10^{37}.$$

The equilibrium constant is given by :

$$\frac{[Zn^{++}] \times [Cu^\circ]}{[Zn^\circ] \times [Cu^{++}]} = K.$$

Now $[Cu^\circ]$ and $[Zn^\circ]$ refer to the solid metallic condition and can therefore be regarded as constant quantities. The equation thus reduces to :

$$\frac{[Zn^{++}]}{[Cu^{++}]} = K.$$

The ratio of the ionic concentrations at equilibrium is shown above to be 2×10^{37}, and this is the equilibrium constant of the reaction. In practice this means that when metallic zinc is added to a solution containing cupric ions, reaction ceases when the ratio of the concentration of the zinc ions produced to the concentration of the copper ions remaining in solution is 2×10^{37}, that is, a practically negligible quantity. For all ordinary purposes this may be taken as the complete removal of cupric ions from solution.

I, 31. Concentration cells.—The electrode potential varies with the concentration of the ions in solution. Hence by bringing two electrodes of the same metal but immersed in solutions containing different concentrations of the ions of the metal into contact, a cell may be formed. Such a cell is termed a *concentration cell.* The e.m.f. of the cell will be the algebraic difference of the two electrode potentials. It may be calculated as follows. At 25° :

$$E \quad \frac{0{\cdot}0591}{n} \log c_1 + E_0 - \frac{0{\cdot}0591}{n} \log c_2 - E_0,$$

$$\frac{0{\cdot}0591}{n} \log \frac{c_1}{c_2}, \text{ where } c_1 > c_2.$$

As an example we may consider the cell :

$$\begin{array}{cccc} \mathrm{Ag} & \begin{array}{c} \mathrm{AgNO_3\,aq.} \\ \mathrm{Ag^+} = 0{\cdot}00475M \end{array} & \begin{array}{c} \mathrm{AgNO_3\ aq.} \\ \mathrm{Ag^+} = 0{\cdot}043M \end{array} & \mathrm{Ag} \end{array}$$

E_1

Assuming no potential difference at the liquid junction :

$$E = E_1 - E_2 = \frac{0{\cdot}0591}{1} \log \frac{0{\cdot}043}{0{\cdot}00475} = \mathit{0{\cdot}056\ volt.}$$

Concentration cells have an obvious application in the determination of the solubility of sparingly soluble salts.

I, 32. Calculation of the e.m.f. of a voltaic cell.—One of the simplest of galvanic cells is the Daniell cell. This consists of a rod of zinc dipping in zinc sulphate solution and a strip of copper in copper sulphate solution ; the two solutions are generally separated by placing one inside a porous pot and the other in the surrounding vessel. The cell may be represented :

$$\mathrm{Zn} \mid \mathrm{ZnSO_4\ aq.} \parallel \mathrm{CuSO_4\ aq.} \mid \mathrm{Cu.}$$

At the zinc electrode, zinc ions pass into solution leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode, rendering it positively charged. By completing the external circuit, the current (electrons) passes from the zinc to the copper. The chemical reactions in the cell are as follows :

(*a*) zinc electrode— $\mathrm{Zn} \rightleftharpoons \mathrm{Zn^{++}} + 2\epsilon,$

(*b*) copper electrode— $\mathrm{Cu^{++}} + 2\epsilon \rightleftharpoons \mathrm{Cu}.$

The net chemical reaction is :

$$\mathrm{Zn} + \mathrm{Cu^{++}} = \mathrm{Zn^{++}} + \mathrm{Cu}.$$

The potential difference at each electrode may be calculated by means of equation (i′), and the e.m.f. of the cell is the algebraic difference of the two potentials, the correct sign being applied to each.

As an example, we may calculate the e.m.f. of the Daniell cell with molar concentrations of zinc ions and cupric ions.

$$E = E_{0(Cu)} - E_{0(Zn)} = +0{\cdot}344 - (-0{\cdot}762) = 1{\cdot}106 \text{ volts.}$$

The small potential difference produced at the contact between the two solutions (the so-called liquid-junction potential) is neglected.

I, 33. Oxidation-reduction cells.—Reduction is accompanied by a gain of electrons and oxidation by a loss of electrons. In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and electrons. If an inert electrode, such as platinum, is placed in a redox system, for example one containing ferric and ferrous ions, it will assume a definite potential indicative of the position of equilibrium. If the oxidation tendency predominates, the system will take electrons from the platinum leaving the latter positively charged ; if, however, the system has reducing properties, electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing power of the system.

To obtain comparative values of the " strengths " of oxidising agents it is necessary, as in the case of the electrode potentials of the metals, to measure under standard experimental conditions the potential difference between the platinum and the solution relative to a standard of reference. The primary standard is the molar hydrogen electrode, and its potential is taken as zero. The standard experimental conditions for the redox system are those in which the ratio of the concentrations of the oxidant to the reductant is unity. Thus for a ferrous-ferric chloride electrode, the redox cell would be :

$$\text{Pt} \left\{ \begin{matrix} \text{Fe}^{+++} \\ \text{Fe}^{++} \end{matrix} \right| \text{H}^{+} \quad \text{H}_2(\text{Pt}).$$

The potential measured in this way is called the *standard oxidation potential.* A selection of these is given in Table XIII. The sign of the potential is that of the electrode.

These oxidation potentials enable one to predict which ions will oxidise or reduce other ions at molar concentrations. The most powerful oxidising agents are at the upper end of the Table and the most powerful reducing agents at the lower end. Thus permanganate ions can oxidise Cl^-, Br^-, I^-, Fe^{++} and $Fe(CN)_6^{----}$ ions ; ferric ions can oxidise AsO_3^{---}, I^-, but not $Cr_2O_7^{--}$ or Cl^- ions. It must be emphasised that

TABLE XIII. STANDARD OXIDATION POTENTIALS AT 25°C

Electrode	*Electrode Reaction*	$E°$
$Co^{+++}, Co^{++}/Pt$	$Co^{+++} + \epsilon \rightleftharpoons Co^{++}$	+1·82
$Pb^{++++}, Pb^{++}/Pt$	$Pb^{++++} + 2\epsilon \rightleftharpoons Pb^{++}$	+1·75
$Ce^{++++}, Ce^{+++}/Pt$	$Ce^{++++} + \epsilon \rightleftharpoons Ce^{+++}$	+1·45
$MnO_4^-, Mn^{++}/Pt$	$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O$	+1·48
$Cl_2, 2Cl^-/Pt$	$Cl_2 + 2\epsilon \rightleftharpoons 2Cl^-$	+1·36
$Cr_2O_7^{--}, 2Cr^{+++}/Pt$	$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O$	+1·3
$IO_3^-, I^-/Pt$	$IO_3^- + 6H^+ + 6\epsilon \rightleftharpoons I^- + 3H_2O$	+1·20
$Br_2, 2Br^-/Pt$	$Br_2 + 2\epsilon \rightleftharpoons 2Br^-$	+1·07
$Fe^{+++}, Fe^{++}/Pt$	$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$	+0·75
$H_3AsO_4, H_3AsO_3/Pt$	$H_3AsO_4 + 2H^+ + 2\epsilon \rightleftharpoons H_3AsO_3 + H_2O$ $AsO_4^{---} + 2H^+ + 2\epsilon \rightleftharpoons AsO_3^{---} + H_2O$	+0·57
$I_2, 2I^-/Pt$	$I_2 + 2\epsilon \rightleftharpoons 2I^-$	+0·54
$Fe(CN)_6^{---}, Fe(CN)_6^{----}/Pt$	$Fe(CN)_6^{---} + \epsilon \rightleftharpoons Fe(CN)_6^{----}$	+0·49
$Cu^{++}, Cu^+/Pt$ $CuCl_2, CuCl/Pt$	$Cu^{++} + 2Cl^- + \epsilon \rightleftharpoons CuCl_2^-$	+0·46
$UO_2^{++}, U^{++++}/Pt$	$UO_2^{++} + 4H^+ + 2\epsilon \rightleftharpoons U^{++++} + 2H_2O$	+0·36
$Sn^{++++}, Sn^{++}/Pt$	$Sn^{++++} + 2\epsilon \rightleftharpoons Sn^{++}$	+0·2
$H_2, 2H^+/Pt$	$2H^+ + 2\epsilon \rightleftharpoons H_2$	0·00
$Cr^{+++}, Cr^{++}/Hg$	$Cr^{+++} + \epsilon \rightleftharpoons Cr^{++}$	−0·41
$S°, S^{--}/Pt$	$S° + 2\epsilon \rightleftharpoons S^{--}$	−0·55

oxidation potentials do not give any information as to the velocity of the reaction; in some cases, the presence of a catalyst is necessary in order that the reaction may proceed with reasonable velocity.

I, 34. Calculation of the oxidation potential.—A reversible oxidation-reduction reaction may be written in the form (*oxidant* = substance in oxidised state, *reductant* = substance in reduced state):

$$\underbrace{\text{Reductant}}_{Red.} \rightleftharpoons \underbrace{\text{Oxidant}}_{Ox.} + n\epsilon$$

The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E_T = E° + \frac{RT}{nF} \log_e \frac{a_{Ox.}}{a_{Red.}} \quad \text{(i)},$$

where E_T is the observed potential of the redox electrode at $T°$, $E°$ is the standard oxidising potential, n the number of electrons or negative charges gained by the oxidant on being converted into the reductant, and $a_{Ox.}$ and $a_{Red.}$ are the activities of the oxidant and reductant respectively. Since activities are often difficult to determine directly, they may be replaced by concentrations; the error thereby introduced is usually of no great importance. The equation therefore becomes :

$$E_T = E^c + \frac{RT}{nF} \log_e \frac{c_{Ox.}}{c_{Red.}} \qquad (\text{i}')$$

Substituting the known values of R and F, and changing from natural logarithms to common or Briggsian logarithms (by multiplying by 2·303), we have for a temperature of 25°C ($T = 288°$) :

$$E_{25°} = E° + \frac{0{\cdot}0591}{n} \log \frac{[Ox.]}{[Red.]} \quad - \qquad (\text{i}'').$$

If the concentrations (or more accurately the activities) of the oxidant and reductant are equal, $E_{25°} = E°$, *i.e.*, the standard oxidation potential. It follows from this expression that, for example, a tenfold change in the ratio of the concentrations of the oxidant to the reductant produces a change in the potential of the system of $0{\cdot}0591/n$ volts.

A simple example will illustrate the application of this formula. Consider the cell :

$$\text{Pt} \; \begin{array}{l} Fe^{+++}\ (0{\cdot}1M) \\ Fe^{++}\ (0{\cdot}001M) \end{array} \; H^+\ (1M), H_2 \;\; \text{Pt}.$$

The e.m.f. is given by (the liquid junction potential between the acid and salt solutions is neglected) :

$$\begin{aligned} E &= E° + \frac{0{\cdot}0591}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]}; \\ &= +\,0{\cdot}75 + 0{\cdot}059 \log \frac{0{\cdot}1}{0{\cdot}001}; \\ &= +\,0{\cdot}75 + 0{\cdot}118 = \mathit{0{\cdot}87\ volt}. \end{aligned}$$

The application of standard oxidation potentials to the calculation of equilibrium constants of simple ionic reactions is illustrated by the following example.

Example 9. Calculate the equilibrium constant of the reaction:

$$Cl_2 + 2Fe^{++} \rightleftharpoons 2Cl^- + 2Fe^{+++}.$$

The equilibrium constant is given by :

$$\frac{[Cl^-]^2 \times [Fe^{+++}]^2}{[Cl_2] \times [Fe^{++}]^2} = K.$$

The reaction may be regarded as taking place in a voltaic cell, the two half cells being a $Cl_2,2Cl^-$ electrode and a Fe^{++}, Fe^{+++} electrode. The reaction is allowed to proceed to equilibrium, the total voltage or e.m.f. of the cell will then be zero, *i.e.*, the potentials of the two electrodes will be equal.

$$E^\circ_{Cl_2,2Cl^-} + \frac{0{\cdot}059}{2}\log\frac{[Cl_2]}{[Cl^-]^2} = E^\circ_{Fe^{++},Fe^{+++}} + \frac{0{\cdot}059}{1}\log\frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Now $E^\circ_{Cl_2,2Cl^-} = 1{\cdot}36$ volts and $E^\circ_{Fe^{++},Fe^{+++}} = 0{\cdot}75$ volt,

$$\therefore \quad \log\frac{[Fe^{+++}]^2 \times [Cl^-]^2}{[Fe^{++}]^2 \times [Cl_2]} = \frac{0{\cdot}61}{0{\cdot}0295} = 20{\cdot}67 = \log K,$$

$$K = 4{\cdot}7 \times 10^{20}$$

The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion. This is in harmony with the practically complete oxidation of a ferrous salt by chlorine, and the stability of a ferric chloride solution.

I, 35. Equilibrium Constant of Oxidation-Reduction Reactions. —The general equation for an oxidation-reduction electrode may be written :

$$pA + qB + rC + \ldots\ldots + N\epsilon = sX + tY + uZ + \ldots\ldots$$

The potential is given by :

$$E = E^\circ + \frac{RT}{nF}\log_e\frac{a_X^s \,.\, a_Y^t \,.\, a_Z^u \ldots\ldots}{a_A^p \,.\, a_B^q \,.\, a_C^r \ldots\ldots},$$

where a refers to activities, and n to the number of electrons involved in the oxidation-reduction reaction. This expression reduces to the following for a temperature of 25°*C* (concentrations are substituted for activities in order to permit of its facile application in practice) :

$$E = E^\circ + \frac{0{\cdot}0591}{n}\log\frac{c_X^s \,.\, c_Y^t \,.\, c_Z^u \ldots\ldots}{c_A^p \,.\, c_B^q \,.\, c_C^r \ldots\ldots}.$$

It is, of course, possible to calculate the influence of change of concentration of certain constituents of the system by the use of the latter equation. Consider, for example, the permanganate reaction :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O.$$

$$E = E^\circ + \frac{0{\cdot}0591}{5}\log\frac{[MnO_4^-] \times [H^+]^8}{[Mn^{++}]}{*} \text{ (at 25°}C\text{)}.$$

---

* More accurately, activities should be employed. The square brackets denote molecular concentrations.

The concentration (or activity) of the water is taken as constant, since it is assumed that the reaction takes place in dilute solution, and the concentration of the water does not change appreciably as a result of the reaction. The equation may be written in the form :

$$E = E^\circ + \frac{0{\cdot}0591}{5} \log \frac{[MnO_4^-]}{[Mn^{++}]} + \frac{0{\cdot}0591}{5} \log [H^+]^8.$$

This enables one to calculate the effect of change in the ratio $[MnO_4^-] / [Mn^{++}]$ at constant hydrogen ion concentration, or to compute the effect of change in the hydrogen ion concentration, other factors being maintained constant. In this particular case difficulties are experienced in the latter calculation owing to the fact that the reduction products of the permanganate ion vary at different hydrogen ion concentrations. In other cases no such difficulties arise, and the calculation may be employed with confidence. Thus in the reaction :

$$H_3AsO_4 + 2H^+ + 2\epsilon \rightleftharpoons H_3AsO_3 + H_2O,$$

$$E = E^\circ + \frac{0{\cdot}0591}{2} \log \frac{[H_3AsO_4] \times [H^+]^2}{[H_3AsO_3]} \text{ (at } 25^\circ C\text{)},$$

$$\text{or } E \quad E^\circ + \frac{0{\cdot}0591}{2} \log \frac{[H_3AsO_4]}{[H_3AsO_3]} + \frac{0{\cdot}0591}{2} \log [H^+]^2.$$

The calculation of equilibrium constants of more complex oxidation-reduction reactions (compare Example *9*, Section **I, 34**) is best illustrated by an actual example.

Example 10. Calculate the equilibrium constant of the reaction :

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightleftharpoons Mn^{++} + 5Fe^{+++} + 4H_2O.$$

The equilibrium constant K is given by :

$$K = \frac{[Mn^{++}] \times [Fe^{+++}]^5}{[MnO_4^-] \times [Fe^{++}]^5 \times [H^+]^8}$$

The term $4H_2O$ is omitted since the reaction is carried out in dilute solution and the water concentration may be assumed constant. The hydrogen ion concentration is taken as molar.

The complete reaction may be divided into two half-cell reactions corresponding to the partial equations :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O \qquad \text{(i)},$$

and

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon \qquad \text{(ii)}.$$

For (i) as an oxidation-reduction electrode, one has :

$$E = E^\circ + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{MnO_4^-}] \times [\mathrm{H^+}]^8}{[\mathrm{Mn^{++}}]},$$
$$= 1{\cdot}48 + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{MnO_4^-}] \times [\mathrm{H^+}]^8}{[\mathrm{Mn^{++}}]}.$$

The partial ionic equation (ii) may be multiplied by 5 in order to balance (i) electrically :

$$5\mathrm{Fe^{++}} \rightleftharpoons 5\mathrm{Fe^{+++}} + 5\epsilon \qquad \text{(ii}'\text{)}.$$

For (ii′) as an oxidation-reduction electrode :

$$E = E^\circ + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{Fe^{+++}}]^5}{[\mathrm{Fe^{++}}]^5},$$
$$= 0{\cdot}75 + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{Fe^{+++}}]^5}{[\mathrm{Fe^{++}}]^5}.$$

Combining the two electrodes into a cell, the e.m.f. will be zero when equilibrium is attained :

$$\textit{i.e.}, 1{\cdot}48 + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{MnO_4^-}] \times [\mathrm{H^+}]^8}{[\mathrm{Mn^{++}}]} = 0{\cdot}75 + \frac{0{\cdot}059}{5}\log\frac{[\mathrm{Fe^{+++}}]^5}{[\mathrm{Fe^{++}}]^5},$$
$$\text{or} \quad \log\frac{[\mathrm{Mn^{++}}] \times [\mathrm{Fe^{+++}}]^5}{[\mathrm{MnO_4^-}] \times [\mathrm{Fe^{++}}]^5 \times [\mathrm{H^+}]^8} = \frac{5(1{\cdot}48 - 0{\cdot}75)}{0{\cdot}059} = 61{\cdot}9.$$
$$K = \frac{[\mathrm{Mn^{++}}] \times [\mathrm{Fe^{+++}}]^5}{[\mathrm{MnO_4^-}] \times [\mathrm{Fe^{++}}]^5 \times [\mathrm{H^+}]^8} = \mathit{1{\cdot}5 \times 10^{62}}.$$

This result clearly indicates that the reaction proceeds to completion.

I, 36. THE IONIC PRODUCT OF WATER

Kohlrausch and Heidweiller (1894) found that the most highly purified water that can be obtained possesses a small but definite electrical conductivity. Water must therefore be slightly ionised in accordance with the equation :

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}{*}.$$

Applying the law of mass action to this equation, one obtains, for any fixed temperature :

$$\frac{a_{\mathrm{H^+}} \times a_{\mathrm{OH^-}}}{a_{\mathrm{H_2O}}} = \frac{[\mathrm{H^+}] \, . \, [\mathrm{OH^-}]}{[\mathrm{H_2O}]} \times \frac{f_{\mathrm{H^+}} \, . \, f_{\mathrm{OH^-}}}{f_{\mathrm{H_2O}}} \qquad \text{a constant,}$$

---

* Strictly speaking the hydrogen ion H^+ exists in water as the hydroxonium ion H_3O^+. The electrolytic dissociation of water should therefore be written :

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}.$$

For the sake of simplicity, the more familiar symbol H^+ will be retained.

where a_x, $[x]$, and f_x refer to the activity, concentration and activity coefficient respectively of the species x. Since water is only slightly ionised, the ionic concentrations will be small and their activity coefficients may be regarded as unity; the activity coefficient of the unionised molecules may also be taken as unity. The expression thus becomes:

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant.}$$

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant. Hence:

$$[H^+] \times [OH^-] = K_w.$$

K_w is the *ionic product of water*. It must be pointed out that the assumption that the activity coefficients of the ions are unity and that the activity coefficient of water is constant applies strictly to pure water and to very dilute solutions (ionic strength $\ngtr$ 0·01); in more concentrated solutions, *i.e.*, in solutions of appreciable ionic strength, the electrical environment affects the activity coefficients of the ions and also the activity of the unionised water. The ionic product of water will then not be constant, but will depend upon the ionic environment. It is, however, difficult to determine the activity coefficients, except under specially selected conditions, so that in practice the ionic product K_w, although not strictly constant, is employed.

The ionic product varies with the temperature, but under ordinary experimental conditions (at about 25°) its value may be taken as 1×10^{-14} with concentrations expressed in gram ions per litre. This is sensibly constant in dilute aqueous solution. If the product of $[H^+]$ and $[OH^-]$ in aqueous solution momentarily exceeds this value, the excess ions will immediately combine to form water. Similarly, if the product of the two ionic concentrations is momentarily less than 10^{-14}, more water molecules will dissociate until the equilibrium value is attained.

The hydrogen and hydroxyl ion concentrations are equal in pure water; therefore:

$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ gram ions per litre at about 25°.

A solution in which the hydrogen and hydroxyl ion concentrations are equal is termed an exactly *neutral solution*. If $[H^+]$ is greater than 10^{-7}, the solution is *acid*, and if less than 10^{-7}, the solution is *alkaline* (or basic). It follows that at ordinary temperatures $[OH^-]$ is greater than 10^{-7} in alkaline solution and less than this value in acid solution.

In all cases the reaction of the solution can be quantitatively expressed by the magnitude of the hydrogen ion (or hydroxonium ion) concentration, or less frequently of the hydroxyl ion concentration, since the following simple relations between $[H^+]$ and $[OH^-]$ exist :

$$[H^+] = \frac{K_w}{[OH^-]}, \text{ and } [OH^-] = \frac{K_w}{[H^+]}.$$

The variation of K_w with temperature is shown in Table XIV.

TABLE XIV. IONIC PRODUCT OF WATER AT VARIOUS TEMPERATURES.

Temp. (°C)	$K_w \times 10^{-14}$	*Temp.* (°C)	$K_w \times 10^{-14}$
0°	0·12	35°	2·09
5°	0·19	40°	2·92
10°	0·29	45°	4·02
15°	0·45	50°	5·48
20°	0·68	55°	7·30
25°	1·01	60°	9·62
30°	1·47		

I, 37. Hydrogen Ion Exponent (pH).—For many purposes, especially when dealing with small concentrations, it is cumbersome to express concentrations of hydrogen and of hydroxyl ions in terms of gram equivalents per litre. A very convenient method was proposed by Sörensen (1909). He introduced the *hydrogen ion exponent* pH defined by the relationships :

$$pH = -\log_{10}[H^+] = \log\frac{1}{[H^+]}, \text{ or } [H^+] = 10^{-pH}.$$

The quantity pH is thus the logarithm of the reciprocal of the hydrogen ion concentration, or is equal to the logarithm of the hydrogen ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions molar (or normal) with respect to hydrogen or hydroxyl ions, can be expressed by a series of positive numbers between 0 and 14. Thus a neutral solution with $[H^+] = 10^{-7}$ has a pH of 7 ; a solution with a molar (or normal) concentration of hydrogen ions has a pH of 0 ($=10^0$) ; and a solution molar with respect to hydroxyl ions has $[H^+] = K_w / [OH^-] = 10^{-14}/10^{\circ} = 10^{-14}$, possesses a pH of 14. A neutral solution is therefore one in which $pH = 7$, an acid solution one in which $pH < 7$, and an alkaline solution one in which $pH > 7$. The greater the hydrogen ion concentration, the smaller is the pH. An alternative definition for a neutral solution is one in which the hydrogen ion and hydroxyl ion concentrations are equal. In an acid solution the hydrogen ion concentration exceeds the hydroxyl ion concentration, whilst in an alkaline or basic solution the hydroxyl ion concentration is greater.

Examples.—(i) Find the pH of a solution of which $[H^+] = 4{\cdot}0 \times 10^{-5}$.

Log $4{\cdot}0 = 0{\cdot}602$, hence log $4{\cdot}0 \times 10^{-5}$ is

$$\bar{5}{\cdot}602 = 0{\cdot}602 - 5 = -4{\cdot}398$$

(the decimal part or mantissa of the logarithm is always positive).

$$pH = -\log[H^+] = -(-4{\cdot}398) = \mathit{4{\cdot}398}.$$

(ii) Find the hydrogen ion concentration corresponding to $pH = 5{\cdot}643$.

$$pH = -\log[H^+] = 5{\cdot}643\ ;\ \therefore \log[H^+] = -5{\cdot}643.$$

This must be written in the usual form containing a negative characteristic and a positive mantissa :

$$\log[H^+] = -5{\cdot}643 = \bar{6}{\cdot}357.$$

Referring to a table of antilogarithms, the number corresponding to the logarithm $0{\cdot}357$ is $2{\cdot}28$; the number corresponding to the logarithm $\bar{6}{\cdot}357$ is accordingly $2{\cdot}28 \times 10^{-6}$.

$[H^+]$ is therefore $\mathit{2{\cdot}28 \times 10^{-6}}$.

(iii) Calculate the pH of a $0{\cdot}01$ molar solution of acetic acid (the degree of dissociation is $12{\cdot}5\%$).

The hydrogen ion concentration is $0{\cdot}125 \times 0{\cdot}01 = 1{\cdot}25 \times 10^{-3}$. Now log $1{\cdot}25 = 0{\cdot}097$;

$$\therefore\ pH = -(-3 + 0{\cdot}097) = \mathit{2{\cdot}903}.$$

The hydroxyl ion concentration may be expressed in a similar way :

$$pOH = -\log_{10}[OH^-] = \log\frac{1}{[OH^-]},\ \text{or}\ [OH^-] = 10^{-pOH}.$$

If one writes the equation :

$$[H^+] \times [OH^-] = K_w = 10^{-14},$$

in the form :

$$\log[H^+] + \log[OH^-] = \log K_w = -14,$$

$$\text{then}\ pH + pOH = pK_w = 14.$$

This relationship should hold for all dilute solutions at about 25°.

Fig. 5 will serve as a useful mnemonic for the relation between $[H^+]$, pH, $[OH^-]$ and pOH in acid and alkaline solution.

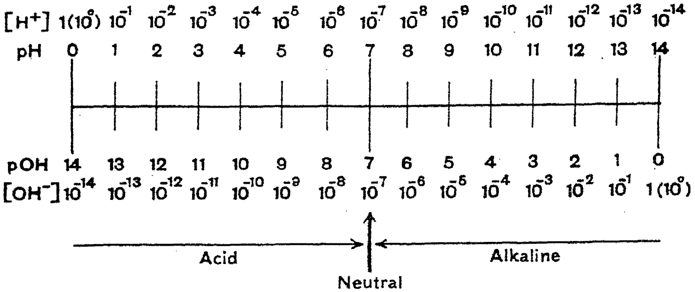
[H+] 1(10⁰) 10⁻¹ 10⁻² 10⁻³ 10⁻⁴ 10⁻⁵ 10⁻⁶ 10⁻⁷ 10⁻⁸ 10⁻⁹ 10⁻¹⁰ 10⁻¹¹ 10⁻¹² 10⁻¹³ 10⁻¹⁴
pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pOH 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
[OH⁻] 10⁻¹⁴ 10⁻¹³ 10⁻¹² 10⁻¹¹ 10⁻¹⁰ 10⁻⁹ 10⁻⁸ 10⁻⁷ 10⁻⁶ 10⁻⁵ 10⁻⁴ 10⁻³ 10⁻² 10⁻¹ 1(10⁰)
Acid
Alkaline
Neutral

Fig. 5

The logarithmic or exponential method has also been found useful for expressing other small numerical quantities which arise in qualitative analysis. These include (i) dissociation constants, (ii) other ionic concentrations, and (iii) solubility products.

(i) For any acid with a dissociation constant of K_a:

$$pK_a = -\log K_a = \log \frac{1}{K_a}$$

Similarly for any base with dissociation constant K_b:

$$pK_b = -\log K_b = \log \frac{1}{K_b}.$$

(ii) For any ion I of concentration [I] :

$$pI = -\log [I] = \log \frac{1}{[I]}.$$

Thus for $[Na^+] = 8 \times 10^{-5}$, $pI = 4{\cdot}1$.

(iii) For a salt with solubility product S :

$$pS = -\log S \quad \log \frac{1}{S}$$

I, 38. Determination of the Hydrogen Ion Concentration.— The hydrogen ion concentration of a solution is of great importance both in pure and in applied chemistry. Two methods are commonly employed for its estimation, (*a*) the colorimetric method and (*b*) the electrometric method.

The Colorimetric Method. In this method one employs what are known as indicators. An *indicator* is a substance which varies in colour according to the hydrogen ion concentration. It is generally a weak organic acid or base and is employed in very dilute solution. The change in colour is usually due either to the production of different tautomeric forms of the original substance or to the formation of coloured ions; the formation of these takes place over a small but definite *p*H range. The hydrogen ion concentrations at which different indicators exhibit their colour change have been determined by direct electrometric methods; the *p*H range over which the indicator is applicable is thus known. Table XV summarises the *p*H values of a number of the more common indicators.

TABLE XV COLOUR CHANGES AND *p*H RANGE OF SOME INDICATORS.

Indicator	*Chemical Name*	*Colour in Acid Solution*	*Colour in Alkaline Solution*	*pH Range*
Brilliant cresyl blue	—	Red-orange	Blue	–0·2–1·0
Meta cresol purple	*m*-Cresol-sulphone-phthalein	Red	Yellow	1·2–2·8
Bromo-phenol blue	Tetrabromo-phenol-sulphone-phthalein	Yellow	Blue	3·0–4·6
Methyl orange	Dimethylamino-azobenzene sulphonic acid (Na salt)	Red	Yellow	3·1–4·4
Bromo-cresol green	Tetrabromo-*m*-cresol-sulphone-phthalein	Yellow	Blue	3·8–5·4
Methyl red	*o*-Carboxy-benzene-azo-dimethylaniline	Red	Yellow	4·2–6·3
Bromo-cresol purple	Dibromo-*o*-cresol-sulphone-phthalein	Yellow	Purple	5·2–6·8
Azolitmin (litmus)	—	Red	Blue	6 –8
Bromo-thymol blue	Dibromo-thymol-sulphone-phthalein	Yellow	Blue	6·0–7·6
Phenol red	Phenol-sulphone-phthalein	Yellow	Red	6·8–8·4
Cresol red	*o*-Cresol-sulphone-phthalein	Yellow	Red	7·2–8·8
Thymol blue	Thymol-sulphone-phthalein	Yellow	Blue	8·0–9·6
Phenol phthalein	Phenol-phthalein	Colourless	Red	8·3–10·0
Thymol phthalein	Thymol-phthalein	Colourless	Blue	9·3–10·5
Nitro-thymol-sulphone-phthalein	Nitro-thymol-sulphone-phthalein	Violet	Yellow	9·2–11·5
Eosin BN	Dibromo-dinitro-fluorescein	Purple	Yellow	10·5–14·0

To determine the *p*H of an unknown solution, a small portion of the latter is first treated with a drop or two of, say, phenolphthalein. If the indicator is colourless, the *p*H of the solution is less than 8·3. If red, the *p*H is greater than 10·0. Let us suppose that the former is the case. Another test is made with methyl orange or bromo-phenol blue. If the solution then assumes the alkaline colour, the *p*H is greater than 4·6. The *p*H of the unknown solution therefore lies between 4·6 and 8·3. Similar tests with methyl red (*p*H range 4·2 — 6·3), bromo-thymol blue (6·0—7·6) and cresol red (7·2—8·8) will show the approximate *p*H, and suggest which indicator should be used in the determination. The limits of the *p*H values of the unknown solution are thus reduced still further.

When an indicator has been found in whose range the *p*H of the solution falls, 0·2 c.c. of the indicator is added to, say, 10 c.c. of the unknown solution. The same volume of indicator is added to 10 c.c. of a series of standard solutions, the *p*H of which differ by regular intervals (0·1—0·2 *p*H) over the *p*H range of the indicator, and the colour compared with that of the unknown solution. The required *p*H is then equal to the value of the standard solution in which the indicator has the same colour as the solution under examination. This procedure requires a series of standard solutions having known hydrogen ion concentrations ; these should be capable of ready preparation and be reproducible. A method for preparing these is described under buffer solutions (Sect. **I, 39**).

The Electrometric Method. The e.m.f. of a concentration cell at 25° is given by (Section **38**) :

$$E = \frac{0{\cdot}0591}{n} \log \frac{c_2}{c_1}\,.$$

If a hydrogen electrode (Sect. **I, 29**) is immersed in the solution the *p*H of which is to be measured, and this half cell coupled with a molar hydrogen electrode by means of a potassium chloride solution bridge in order to eliminate liquid junction potential, the e.m.f. of the resultant cell :

$$\mathrm{Pt} \mid \underset{a\,=\,1}{\mathrm{H_2, H^+}} \parallel \underset{a\,=\,x}{\mathrm{H_2, H^+}} \mid \mathrm{Pt},$$

may be measured.

$$\begin{aligned} \text{Here}\quad E &= \frac{0{\cdot}0591}{1} \log \frac{1}{[\mathrm{H^+}]} \quad (\text{at } ca.\ 25°), \\ &= 0{\cdot}0591\, p\mathrm{H}. \\ p\mathrm{H} &= E/0{\cdot}0591. \end{aligned}$$

The use of the molar hydrogen electrode as a standard electrode or half cell presents certain practical difficulties. It is usual to employ some form of the calomel electrode as a secondary standard half cell. A *calomel electrode* is one in which mercury and calomel are covered with a potassium chloride solution of definite concentration; this may be 0·1*N*, *N*, 3·5*N* or saturated. The potassium chloride solution must be saturated with calomel. The potential of, say, the saturated calomel electrode (*i.e.*, that prepared with saturated potassium chloride solution) must first be determined with reference to the molar hydrogen electrode. Let this value be designated $E_{cal.\ (sat.)}$. For the measurement of hydrogen ion concentration one then employs the cell:

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2,\ \text{KCl(satd.)} \parallel \text{H}^+,\ \text{H}_2 \mid \text{Pt}.$$

Let the resultant e.m.f. be $E_{obs.}$ One then has at 25°:

$$E_{obs.} = E_{cal.\ (sat).} - 0{\cdot}0591 \log [\text{H}^+],$$

$$pH = \frac{E_{obs.} - E_{cal.\ (sat.)}}{0{\cdot}0591}$$

The value of $E_{cal.\ (sat.)}$ is 0·246 volt at 25°.

A simple form of calomel electrode suitable for elementary work is illustrated in Fig. 6. It consists of a glass vessel provided with a bent side tube *A* and another side tube *B*, over the end of which a piece of rubber tubing is placed which can be closed by a spring or screw clip. Electrical connection with the electrode is made by means of a platinum wire, sealed through a glass tube *C*; the latter contains a little pure mercury into which an amalgamated copper wire dips. To set up the electrode a saturated solution of analytically pure potassium chloride containing some solid salt is first prepared. Pure mercury to a depth of about 0·5 cm. is placed in the bottom of the dry electrode vessel; the mercury is then covered with a layer of calomel paste. The latter is prepared by rubbing pure calomel, mercury and saturated potassium chloride solution together in a mortar; the supernatant liquid is poured off and the rubbing process repeated twice

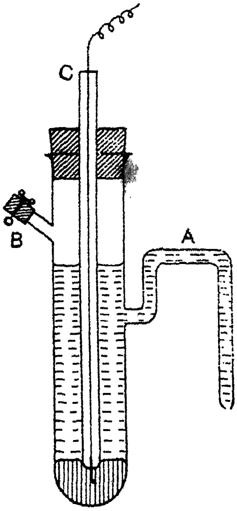

Fig. 6

with fresh quantities of saturated potassium chloride solution. The rubber stopper carrying the glass tube and platinum wire is then inserted, care being taken that the platinum wire dips into the mercury. The vessel is then filled with a saturated solution of potassium chloride (previously saturated with calomel by shaking with the solid salt) by drawing in the solution through the bent tube A and then closing the rubber tube B with a clip. The electrode is then ready for use.

The preparation of reproducible hydrogen electrodes is a comparatively tedious process. The electrode cannot be employed in the presence of reducible substances or of ions which have positive electrode potentials (see Table XIII), such as copper, silver and gold. Biilmann (1921) has introduced the *quinhydrone electrode* ; this renders the determination of *p*H a rapid and simple process and does not involve the use of hydrogen gas. The underlying theory is as follows. Let us consider the reversible reduction of quinone to quinhydrone in acid solution :

$$C_6H_4O_2 + 2H^+ + 2\epsilon \rightleftharpoons C_6H_4(OH)_2.$$

This is a reversible oxidation-reduction system and the potential of an inert electrode, such as platinum, immersed in the system is given by :

$$\begin{aligned} E &= E_0 + \frac{RT}{2F}\log_e \frac{a_Q \cdot a_{H^+}^2}{a_{H_2Q}} , \\ &= E_0 - \frac{RT}{2F}\log_e \frac{a_{H_2Q}}{a_Q} + \frac{RT}{F}\log_e a_{H^+} , \end{aligned}$$

where a_Q, a_{H^+}, a_{H_2Q} are the activities of the quinone, hydrogen ions and hydroquinone respectively, and E_0 is the standard potential referred to the molar hydrogen electrode. If the solution contains equi-molecular amounts of quinone and hydroquinone, the ratio of the activities may be regarded as constant :

$$E = E_0 + \frac{RT}{F}\log_e a_{H^+} \qquad \text{(i).}$$

The sparingly soluble substance quinhydrone is a molecular compound of quinone and hydroquinone, $C_6H_4O_2.C_6H_4(OH)_2$, and dissociates into the two components when dissolved in water ; it follows, therefore, that in the *p*H range over which this compound is stable, equation (i) holds. It may therefore be employed for the determination of *p*H. E_0 has been determined in the usual manner by direct reference to the molar hydrogen electrode, and has a value of 0·704 volt at 18° and 0·699 volt at 25°. By making the usual substitution for the known values of the constants in equation (i), one obtains at 25° :

$$E = 0{\cdot}699 + 0{\cdot}0591 \log a_{\mathrm{H}^+}.$$

Thus the potential of the quinhydrone electrode changes with the hydrogen ion activity in a manner which is exactly similar to that of the hydrogen electrode.

For convenience, a calomel electrode replaces the molar hydrogen electrode as the other half cell. The complete cell is then :

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl\ (satd.)} \parallel \mathrm{Solution,\ quinhydrone} \mid \mathrm{Pt}.$$

The potential of the saturated calomel electrode, $E_{cal.\,(sat.)}$, against the molar hydrogen electrode is 0·246 volt at 25°.

Hence
$$\begin{aligned} E_{obs.} &= E_{quinhydrone} - E_{cal.\,(sat.)}, \\ &= 0{\cdot}699 + 0{\cdot}0591 \log [\mathrm{H}^+] - 0{\cdot}246, \\ &= 0{\cdot}453 + 0{\cdot}0591 \log [\mathrm{H}^+]. \end{aligned}$$

$$-\log [\mathrm{H}^+] = p\mathrm{H} = \frac{0{\cdot}453 - E_{obs.}}{0{\cdot}0591}.$$

To carry out the determination of the hydrogen ion concentration of a solution, about 1 gram of quinhydrone per 100 c.c. of the solution is added, and the solution stirred. A bright platinum electrode is immersed in the solution and the quinhydrone electrode combined in a cell with a saturated calomel electrode ; a saturated solution of potassium chloride may be used as the salt bridge. The e.m.f. of the cell is determined, and the pH calculated.

An alternative method is to use a solution of known pH as standard and to combine the two quinhydrone electrodes into a concentration cell :

$$\mathrm{Pt} \left| \begin{array}{l} \text{Solution of unknown} \\ p\text{H, quinhydrone} \end{array} \right\| \begin{array}{l} \text{Solution of known} \\ p\text{H, quinhydrone} \end{array} \quad \mathrm{Pt}.$$

Then
$$E_{obs.} = 0{\cdot}0591 \log \frac{c_2}{c_1}$$

where c_2 and c_1 are the respective hydrogen ion concentrations.

$$p\mathrm{H}_2 = \frac{p\mathrm{H}_1 - E_{obs.}}{0{\cdot}0591},$$

where $p\mathrm{H}_2$ refers to c_2 and $p\mathrm{H}_1$ to c_1. If $p\mathrm{H}_2$ is known, $p\mathrm{H}_1$ can be readily calculated.

The two quinhydrone electrodes may be connected by a salt bridge containing saturated potassium chloride solution; an apparatus similar to that shown in Fig. 2 (Sect. **I, 28**) may be employed except that the platinum electrodes should be smaller, say, 1 cm. square. The e.m.f. is measured by a potentiometric method based upon the Poggendorff compensation principle; details of this will be found in textbooks of physics or of physical chemistry.

It must be pointed out that the quinhydrone electrode cannot be employed in alkaline solution in which the *p*H is greater than 8, for the ratio of quinone to hydroquinone is no longer unity.

I, 39. Buffer Solutions.—A solution of 0·0001*M* hydrochloric acid should give a *p*H equal to 4, but the solution is extremely sensitive to traces of alkali from the glass of the containing vessel and to ammonia from the air. Likewise a 0·0001*M* solution of sodium hydroxide, which should have a *p*H of 10, is sensitive to traces of carbon dioxide from the atmosphere. Aqueous solutions of potassium chloride and of ammonium acetate have a *p*H of about 7. The addition of 1 c.c. of molar hydrochloric acid to 1 litre of the solution results in a change of *p*H to 3 in the former case and in very little change in the latter. The resistance of a solution to changes in hydrogen ion concentration upon the addition of acid or alkali is termed *buffer action*; a solution which possesses such properties is known as a *buffer solution.* It is said to possess "reserve acidity" and "reserve alkalinity." Solutions of which the *p*H values (determined by reference to the hydrogen electrode) are known, which can be readily prepared and which are unaffected by small additions of alkali or acid, are required for the colorimetric determination of hydrogen ion concentration and for other purposes.

Buffer mixtures usually consist of solutions containing a mixture of a weak acid or base and its salt. In order to understand buffer action, let us study first the equilibrium between a weak acid and its salt. The dissociation of a weak acid HA is given by:

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-,$$

and its magnitude is controlled by the value of the dissociation constant K_a:

$$\frac{a_{\mathrm{H}^+} \times a_{\mathrm{A}^-}}{a_{\mathrm{HA}}} = K_a\,, \quad or \quad a_{\mathrm{H}^+} = \frac{a_{\mathrm{HA}}}{a_{\mathrm{A}^-}} \times K_a \qquad \text{(i),}$$

where a_X refers to the activity of the species X. The expression may be approximated by writing concentrations for activities (strictly speaking, it will be recalled (Section **I, 12**), activity = concentration × activity coefficient) :

$$[H^+] = \frac{[HA]}{[A^-]} \times K_a \qquad \text{(ii).}$$

This equilibrium applies to a mixture of an acid HA and its salt, say, MA. If the concentration of the acid be c_a and that of the salt be c_s, then the concentration of the undissociated portion of the acid is $c_a - [H^+]$. The solution is electrically neutral, hence $[A^-] = c_s + [H^+]$ (the salt is completely dissociated). Substituting these values in the equilibrium equation (ii) :

$$[H^+] = \frac{c_a - [H^+]}{c_s + [H^+]} \times K_a \qquad \text{(iii).}$$

This is a quadratic equation for $[H^+]$, and may be solved in the usual manner. It can, however, be simplified by introducing the following approximation. In a mixture of a weak acid and its salt, the dissociation of the acid is repressed by the common ion effect, and $[H^+]$ may be taken as negligibly small by comparison with c_a and c_s. Equation (iii) then reduces to :

$$[H^+] = \frac{c_a}{c} \,.\, K_a, \quad \textit{or} \quad [H^+] = \frac{[\text{Acid}]}{[\text{Salt}]} \times K_a \qquad \text{(iv),}$$

$$\textit{or}\ pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{(v).}$$

Similarly for a mixture of a weak base of dissociation constant K_b and its salt with a strong acid :

$$[OH^-] = \frac{[\text{Base}]}{[\text{Salt}]} \times K_b \qquad \text{(vi),}$$

$$\textit{or} \qquad pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad \text{(vii).}$$

Let us confine our attention to the case in which the concentrations of the acid and its salt are equal, *i.e.*, of a half neutralised acid. Then $pH = pK_a$. Thus the pH of a half neutralised solution of a weak acid is equal to the negative logarithm of the dissociation constant of the acid. For acetic acid $K_a = 1{\cdot}82 \times 10^{-5}, pK_a = 4{\cdot}74$; a half neutralised solution of, say, 0·1*M* acetic acid will have a *p*H of 4·74. If one adds a small concentration of H⁺ ions to such a solution, the former will combine with the acetate ions to form undissociated acetic acid...

$$H^+ + C_2H_3O_2^- \rightleftharpoons H.C_2H_3O_2.$$

Similarly, if a small concentration of hydroxyl ions be added, the latter will combine with the hydrogen ions arising from the dissociation of the acetic acid and form unionised water ; the equilibrium will be disturbed and more acetic acid will dissociate to replace the hydrogen ions removed in this way. In either case, the concentrations of the acetic acid and acetate ion (or salt) will not be appreciably changed. It follows from equation (v) that the *p*H of the solution will not be materially affected.

The solution containing equal concentrations of acid and salt, or a half neutralised solution of the acid, has the maximum buffer capacity. Other mixtures also possess considerable buffer capacity, but the *p*H will differ slightly from the half neutralised acid. Thus in a quarter neutralised solution of acid, [Acid] = 3 [Salt] :

$$\begin{aligned} pH &= pK_a + \log 1/3 = pK_a + \bar{1}{\cdot}52, \\ &= pK_a - 0{\cdot}48. \end{aligned}$$

For a three-quarter neutralised acid, [Salt] = 3 [Acid] :

$$\begin{aligned} pH &= pK_a + \log 3, \\ &= pK_a + 0{\cdot}48. \end{aligned}$$

In general, it may be stated that the buffering capacity is maintained for mixtures within the range 1 acid : 10 salt and 10 acid : 1 salt. The approximate *p*H range of a weak acid buffer is :

$$pH = pKa \pm 1 ;$$

the concentration of the acid is usually of the order 0·05 — 0·2 molar. Similar remarks apply to weak bases.

The preparation of a buffer solution of a definite *p*H is a simple process if the acid (or base) of appropriate dissociation constant is found ; small variations in *p*H are obtained by variations in the ratio of the acid to the salt concentration. One example is given in Table XVI.

TABLE XVI. *p*H OF ACETIC ACID—SODIUM ACETATE BUFFER MIXTURES.*

10 c.c. mixtures of *x* c.c. of 0·2*M* acetic acid and *y* c.c. of 0·2*M* sodium acetate.

Acetic Acid (x *c.c.*)	*Sodium Acetate* (y *c.c.*)	p*H*
9·0	1·0	3·72
8·0	2·0	4·05
7·0	3·0	4·27
6·0	4·0	4·45
5·0	5·0	4·63
4·0	6·0	4·80
3·0	7·0	4·99
2·0	8·0	5·23
1·0	9·0	5·57

Before leaving the subject of buffer solutions it is necessary to draw attention to a possible erroneous deduction from equation (v), namely, that the hydrogen ion concentration of a buffer solution is dependent only upon the ratio of the concentrations of acid and salt and upon K_a, and not upon the actual concentrations; otherwise expressed, that the *p*H of such buffer mixture should not change upon dilution with water. This is approximately although not strictly true. In deducing equation (ii) concentrations have been substituted for activities, a step which is not entirely justifiable except in dilute solution. Theoretically, the expression controlling buffer action is :

$$a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a = \frac{c_a f_a}{c_s f_{A^-}} \times K_a,$$

where *a* and *f* refer to activities and activity coefficients respectively of the species indicated in the subscript. The activity coefficient f_a of an undissociated acid is approximately unity in dilute aqueous solution. The activity coefficient of the ion f_{A^-}, however, generally increases with decreasing ion concentration, so that when a buffer solution is diluted, f_{A^-} increases and consequently a_{H^+} will decrease. For most practical purposes the change is small, but for exact work the change must be taken into account. The addition of salts to a buffer mixture results in a change of the ionic strength of the solution ; this will affect the activity coefficients of the ions and therefore the *p*H of the solution. Indeed, in all buffer solutions a correction should, strictly speaking, be applied for the ionic strength of the solution.

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* Britton, *Hydrogen Ions*, 1932, p. 220.

I, 40. HYDROLYSIS OF SALTS

Salts may be divided into four main groups :

I, those derived from the strong acids and strong bases, *e.g.*, potassium chloride ;

II, those derived from weak acids and strong bases, *e.g.*, sodium acetate ;

III, those derived from strong acids and weak bases, *e.g.*, ammonium chloride ; and

IV, those derived from weak acids and weak bases, *e.g.*, ammonium formate or aluminium acetate.

When any of these is dissolved in water, the solution, as is well known, is not always neutral in reaction. Interaction occurs with the ions of water and the resultant solution may be neutral, acid or alkaline according to the nature of the salt.

With an aqueous solution of a salt of group I, neither the anions have any tendency to combine with hydrogen ions nor the cations with the hydroxyl ions of water. The equilibrium between the hydrogen and hydroxyl ions in water :

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{(i)},$$

is therefore not disturbed and the solution remains neutral.

Consider, however, a salt MA derived from a weak acid HA and a strong base BOH (group II). The salt is completely dissociated in aqueous solution :

$$MA \rightleftharpoons M^+ + A^-.$$

A very small concentration of hydrogen and hydroxyl ions, originating from the small but finite ionisation of water, will be initially present. HA is a weak acid, that is, it is ionised only to a small degree ; the concentration of A^- ions which can exist in equilibrium with H^+ ions is accordingly small. In order to maintain the equilibrium the large initial concentration of A^- ions must be reduced by combination with H^+ ions to form unionised HA :

$$H^+ + A^- \rightleftharpoons HA \qquad \text{(ii)}.$$

The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water ; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA, consequently the hydroxyl ion concentration of the solution will increase and the solution will react alkaline.

The net result is that the anions of the salt react with the hydrogen ions of water yielding the weak acid HA, and there is an increase in the concentration of hydroxyl ions over that present in water.

It is usual in writing equations involving equilibria between completely dissociated and slightly dissociated or sparingly soluble substances to employ the ions of the former and the molecules of the latter. The reaction is therefore written :

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad \text{(iii)}.$$

This equation can also be obtained by combining (i) and (ii) since both equilibria must coexist.

This interaction between the ion (or ions) of a salt and the ions of water is called *hydrolysis*. Formerly the chemical reaction was written :

$$MA + H_2O \rightleftharpoons MOH + HA,$$

or as :

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Base} + \text{Acid}.$$

The reaction of the solution was clearly dependent upon the relative strength of MOH and HA. This led to the definition of hydrolysis as the decomposition of a salt by water into an acid and a base.

Let us now study the salt of a strong acid and a weak base (group III). Here the initial high concentration of cations M^+ will be reduced by combination with the hydroxyl ions of water to form the little ionised MOH until the equilibrium :

$$M^+ + OH^- \rightleftharpoons MOH \qquad \text{(iv)},$$

is attained. The hydrogen ion concentration of the solution will thus be increased and the solution will react acid. The hydrolysis is here represented by :

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(v)}.$$

For salts of group IV in which both the acid and base are weak, two reactions will occur simultaneously :

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(vi)},$$
$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \text{(vii)}.$$

The reaction of the solution will clearly depend upon the relative strengths or dissociation constants of the acid and base. If they are equal in strength, the solution will be neutral ; if $K_a > K_b$, it will be acid, and if $K_b > K_a$, it will be alkaline.

Having considered all the possible cases, we are now in a position to give a more general definition of hydrolysis.

Hydrolysis is the interaction between the ion (or ions) of a salt and the ions of water with the production of (*a*) a weak acid *or* a weak base or (*b*) of both a weak acid *and* a weak base.

I, 41. Hydrolysis Constant and Degree of Hydrolysis.

Case 1. Salt of a Weak Acid and a Strong Base. The equilibrium in solution of a salt MA may be represented by :

$$M^+ + A^- + H_2O \rightleftharpoons M^+ + OH^- + HA,$$

or by

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad \text{(i)}.$$

Applying the law of mass action, one obtains :

$$\frac{a_{OH^-} \times a_{HA}}{a_{A^-}} = \frac{[OH^-].[HA]}{[A^-]} \times \frac{f_{OH^-} \cdot f_{HA}}{f_{A^-}} = K_h \qquad \text{(ii)}$$

where *a, f* and [ ] refer to activities, activity coefficients and concentrations respectively, and K_h is the *hydrolysis constant.* The solution is assumed to be dilute ; the activity of the unionised water may be then taken as constant. In dilute solutions, the ionic strength is small, and the approximation that the activity coefficient of the unionised acid is unity and also $f_{OH^-} / f_{A^-} = 1$ may be introduced. Equation (ii) then reduces to :

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} \qquad \text{(iii)}.$$

This is often written in the form :

$$K_h = \frac{[Base] \times [Acid]}{[Unhydrolysed\ Salt]} \qquad \text{(iv)} ;$$

the free strong base and the unhydrolysed salt are completely ionised and the acid is very little dissociated.

The *degree of hydrolysis* is the fraction of each gram molecule hydrolysed at equilibrium. Let 1 gram mol of salt be dissolved in V litres of solution and let x be the degree of hydrolysis. The concentrations in gram mols or gram ions per litre are :

$$[OH^-] = x/V \ ; \ [HA] = x/V \text{ and } [A^-] = 1 - x/V.$$

Substituting in (iii) :

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{x/V \times x/V}{(1-x)/V} = \frac{}{(1-x)V} \qquad \text{(v)}.$$

This expression enables one to calculate the degree of hydrolysis from the value of the hydrolysis constant at the dilution V. It is evident that as V increases the degree of hydrolysis x must increase.

The two equilibria :

$$H_2O \rightleftharpoons H^+ + OH^-,$$

and

$$HA \rightleftharpoons H^+ + A^-,$$

must coexist with the hydrolytic equilibrium :

$$A^- + H_2O \rightleftharpoons HA + OH^-.$$

Hence the two relationships :

$$[H^+] \times [OH^-] = K_w$$

and

$$[H^+] \times [A^-] \,/\, [HA] = K_a,$$

must hold in the same solution as :

$$[OH^-] \times [HA] \,/\, [A^-] = K_h.$$

But $\dfrac{K_w}{K_a} = \dfrac{[H^+] \times [OH^-] \times [HA]}{[H^+] \times [A^-]} = \dfrac{[OH^-] \times [HA]}{[A^-]} = K_h,$

therefore $$K_w \,/\, K_a = K_h \qquad \text{(vi)},$$

or $$pK_h = pK_w - pK_a \qquad \text{(vii)}.$$

The hydrolysis constant is thus related to the ionic product of water and the ionisation constant of the acid. Since K_a varies slightly and K_w varies considerably with temperature, K_h and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

Example 11. Calculate (1) the hydrolysis constant, (2) the degree of hydrolysis and (3) the hydrogen ion concentration of a 0·01 molar solution of sodium acetate at the laboratory temperature.

$$K_h = \frac{K_w}{K_a} = \frac{1{\cdot}0 \times 10^{-14}}{1{\cdot}82 \times 10^{-5}} = 5{\cdot}5 \times 10^{-10}$$

The degree of hydrolysis x is given by :

$$K_h = \frac{x^2}{(1 - x)\,V}$$

Substituting for K_h and V ($= 1/c$), one obtains :

$$5{\cdot}5 \times 10^{-10} = \frac{x^2 \times 0{\cdot}01}{(1 - x)} \;.$$

Solving this quadratic equation for x, $x = 0{\cdot}000235$ or $0{\cdot}0235\%$.

$$\underset{1\text{ mol}}{C_2H_3O_2^-} + H_2O \rightleftharpoons \underset{1\text{ mol}}{H.C_2H_3O_2} + \underset{1\text{ mol}}{OH^-}.$$

If the solution were completely hydrolysed, the concentration of acetic acid produced would be $0{\cdot}01M$. But the degree of hydrolysis is $0{\cdot}0235\%$, therefore the concentration of acetic acid is $2{\cdot}35 \times 10^{-6}M$. This is also equal to the hydroxyl ion concentration produced, *i.e.*, pOH $= 5{\cdot}63$.

$$pH = 14{\cdot}0 - 5{\cdot}63 = \mathit{8{\cdot}37}.$$

The pH may also be computed from equation (ix) below:

$$\begin{aligned} pH &= 1/2\,pK_w + 1/2\,pK_a + 1/2\log c, \\ &= 7{\cdot}0 \quad + \quad 2{\cdot}37 \quad + 1/2\,(-2) \quad = \mathit{8{\cdot}37}. \end{aligned}$$

The hydrogen ion concentration of a solution of a hydrolysed salt can be readily computed. The amounts of HA and OH^- ions formed as a result of hydrolysis are equal, therefore in a solution of the pure salt in water $[HA] = [OH^-]$.

If the concentration of the salt is c gram mols per litre, then:

$$\frac{[HA] \times [OH^-]}{[A^-]} = \frac{[OH^-]^2}{c} = K_h = \frac{K_w}{K_a},$$

$$\text{and} \qquad [OH^-] = \sqrt{\frac{c.K_w}{K_a}} \qquad \text{(vii)},$$

$$or \quad [H^+] = \sqrt{K_w \,.\, K_a} \quad \text{since } [H^+] = K_w\,/\,[OH^-] \qquad \text{(viii)};$$

$$\therefore \qquad pH = 1/2pK_w + 1/2\,pK_a + 1/2\log c^* \qquad \text{(ix)}.$$

Equation (ix) can be employed for the calculation of the pH of a solution of a salt of a weak acid and strong base. Thus the pH of a $0{\cdot}05M$ solution of sodium benzoate is given by:

$$pH = 7{\cdot}0 + 2{\cdot}10 + 1/2(-1{\cdot}30) = 8{\cdot}45.$$

(Benzoic acid: $K_a = 6{\cdot}37 \times 10^{-5}$; $pK_a = 4{\cdot}20$.)

Such a calculation will provide useful information as to the indicator which should be employed in the titration of a weak acid and strong base. An explanation is thus given for the use of phenol phthalein (pH range $8{\cdot}3 - 10{\cdot}0$) in the titration of benzoic (or acetic) acid with strong bases.

Case 2. Salt of a Strong Acid and a Weak Base. The hydrolytic equilibrium is represented by:

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(x)}.$$

By applying the law of mass action along the lines of Case 1, the following equations are obtained:

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[\text{Acid}] \times [\text{Base}]}{[\text{Unhydrolysed Salt}]} = \frac{K_w}{K_b} \qquad \text{(xi)},$$

$$= \frac{x^2}{(1 - x)V} \qquad \text{(xii)}.$$

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* To be consistent one should write $p_c =$ · $\log c$.

K_b is the dissociation constant of the base. Furthermore, since [MOH] and [H⁺] are equal (equation (x)),

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[H^+]^2}{c} = \frac{K_w}{K_b},$$

$$[H^+] = \sqrt{\frac{c.K_w}{K_b}}$$

or $$pH = 1/2\, pK_w - 1/2\, pK_b - 1/2 \log c \qquad \text{(xiii)}.$$

Equation (xiii) can be applied to the calculation of the pH of the solutions of salts of strong acids and weak bases. Thus the pH of a $0{\cdot}2M$ solution of ammonium chloride is :

$$pH = 7{\cdot}0 - 2{\cdot}37 - 1/2\ (-0{\cdot}70) = 4{\cdot}98.$$

(Ammonium hydroxide : $K_b = 1{\cdot}85 \times 10^{-5}$; $pK_b = 4{\cdot}74$.)

The reason for the use of methyl orange (pH range 3·1—4·4) or of methyl red (pH range 4·2—6·3) in the titration of ammonia solutions with strong acids is now apparent.

Case 3. Salt of a Weak Acid and a Weak Base. The hydrolytic equilibrium is expressed by the equation :

$$M^+ + A^- + H_2O \rightleftharpoons MOH + HA \qquad \text{(xiv)}.$$

Applying the law of mass action and taking the activity of unionised water as unity :

$$K_h = \frac{a_{MOH} \cdot a_{HA}}{a_{M^+} \cdot a_{H^+}} = \frac{[MOH] . [HA]}{[M^+] . [A^-]} \times \frac{f_{MOH} \cdot f_{HA}}{f_{M^+} \cdot f_{A^-}} \qquad \text{(xv)}.$$

By the usual approximations, that is, by assuming that the activity coefficients of the unionised molecules and, less justifiably, of the ions are unity, the following approximate equation is obtained :

$$K_h = \frac{[MOH] \times [HA]}{[M^+] \times [A^-]} \qquad \text{(xvi)},$$

$$= \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed Salt}]^2} \qquad \text{(xvii)}.$$

If x is the degree of hydrolysis of 1 gram mol of the salt dissolved in V litres of solution, then the individual concentrations are :

$$[MOH] = [HA] = x/V; [M^+] = [A^-] = (1 - x)/V.$$

Substituting these values in (xvi) :

$$K_h = \frac{x/V \,.\, x/V}{(1-x)/V\ (1-x)/V} = \frac{x^2}{(1 - x)^2} \qquad \text{(xviii)}.$$

The degree of hydrolysis and consequently the pH is independent of the concentration of the salt solution.*

As in Case 1 the expressions :

$$K_w = [H^+] \times [OH^-],$$

$$K_a = \frac{[H^+] \times [A^-]}{[HA]}, \text{ and } K_b = \frac{[M^+] \times [OH^-]}{[MOH]},$$

hold simultaneously with the equation (xiv) for the hydrolytic equilibrium. By substitution in the last-named equation, it can be readily shown that :

$$K_h = K_w \,/\, K_a \times K_b \qquad \text{(xix)},$$

or

$$pK_h = pK_w - pK_a - pK_b \qquad \text{(xx)}.$$

This expression enables one to compute the value of x from the dissociation constants of the acid and the base.

The hydrogen ion concentration of the hydrolysed solution is calculated in the following manner :

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \quad \frac{x/V}{(1 - x)/V} = K_a \times \frac{x}{(1 - x)}$$

But $x/(1 - x) = \sqrt{K_h}$ (by equation (xviii)),

$$\therefore \; [H^+] = K_a . \sqrt{K_h} = \sqrt{\frac{K_w \times K_a}{K_b}} \qquad \text{(xxi)},$$

or

$$pH = 1/2\, pK_w + 1/2\, pK_a - 1/2\, pK_b \qquad \text{(xxii)}.$$

If the ionisation constants of the acid and base are equal, that is, $K_a = K_b$, $p\text{H} = 1/2 pK_w = 7{\cdot}0$, and the solution is neutral although hydrolysis may be considerable. If $K_a > K_b$, $p\text{H} < 7$ and the solution is acid, but when $K_b > K_a$, $p\text{H} > 7$ and the solution reacts alkaline.

The pH of a solution of ammonium acetate is given by :

$$pH = 7{\cdot}0 + 2{\cdot}37 - 2{\cdot}37 = 7{\cdot}0,$$

i.e., the solution is approximately neutral. On the other hand, for any solution of ammonium formate :

$$pH = 7{\cdot}0 + 1{\cdot}88 - 2{\cdot}37 = 6{\cdot}51,$$

(Formic acid : $K_a = 1{\cdot}77 \times 10^{-4}$; $pK_a = 3{\cdot}75$.)

i.e., the solution reacts slightly acid.

I,42. The Distribution Law.—It is a well-known fact that certain substances are more soluble in some solvents than in others. Thus iodine is very much more soluble in carbon disulphide, chloroform or carbon tetrachloride than it is in water. Furthermore, when certain liquids such as carbon disulphide and water, and also ether and water, are shaken together in a vessel and the mixture allowed to stand, the two liquids separate out into two layers. Such liquids are said to be immiscible (carbon disulphide and water) or partially miscible (ether and water), according as to whether they are almost insoluble or partially soluble in one another. If iodine is shaken with a mixture of carbon disulphide and water and then allowed to settle, the iodine will be found to be distributed between the two solvents. A state of equilibrium exists between the solution of iodine in carbon disulphide and the solution of iodine in water. It has been found that when the amount of iodine is varied, the ratio of the concentrations is constant at any given temperature. That is :

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* This applies only if the original assumptions as to activity coefficients are justified.

$$\frac{\text{Concentration of iodine in carbon disulphide}}{\text{Concentration of iodine in water}} = \frac{C_2}{C_1} = K.$$

The constant K is known as the *partition* or *distribution coefficient.* Some early (and therefore approximate) experimental results are collected below.

Grams of iodine in 10 c.c. of CS_2 (C_2)	*Grams of iodine in 10 c.c. of H_2O (C_1)*	$K = \frac{C_2}{C_1}$
1·76	0·0041	420
1·29	0·0032	400
0·66	0·0016	410
0·41	0·0010	410

It is important to note that the ratio C_2/C_1 is constant only when the dissolved substance has the same molecular weight in both solvents. The *distribution law* may be formulated: when a solute distributes itself between two immiscible solvents, there exists for each molecular species, at a given temperature, a constant ratio of distribution between the two solvents, and this distribution ratio is independent of any other molecular species which may be present.

The distribution law has a number of applications in analysis.

(*a*) *Removal of bromine and iodine from aqueous solutions.* When an aqueous solution of iodine is shaken with carbon disulphide, the concentration of iodine in the resultant carbon disulphide layer is about 400 times that in the water. The carbon disulphide may be removed with the aid of a separating funnel and the process repeated. In this way the concentration of iodine in the aqueous solution can be reduced to a very small value, although theoretically it cannot be completely removed. With carbon tetrachloride the distribution coefficient is 85.

Use is made of the partition principle in the detection of bromides (Sect. **IV, 15,** reaction *5*), of iodides (Sect. **IV, 16,** reaction *4*), and in the detection of bromides and iodides in the presence of each other (Sect. **IV, 44,** *7*).

(*b*) *Various tests in qualitative analysis.* (i) Perchromic acid (Sect. **IV, 33,** reaction *4*) is more soluble in ether than in water; by shaking the dilute aqueous solution with ether, a concentrated solution in the latter solvent is obtained, and the presence of chromate or of hydrogen peroxide is indicated by the blue colour.

(ii) The compound ammonium cobaltothiocyanate, $(NH_4)_2[Co(CNS)_4]$, produced by the action of a concentrated solution of ammonium thiocyanate upon a cobaltous salt (see Section **III, 24,** reaction *6*), is more soluble in amyl alcohol than in water; the blue colouration of the amyl alcohol layer, due to the formation of a concentrated solution of this compound, is a sensitive and characteristic test for cobalt.

(iii) " Ferric thiocyanate " $Fe[Fe(CNS)_6]$ (see Section **III, 20,** reaction *10*) has a greater solubility in ether than in water, and yields a characteristic red solution in the former solvent. This is the basis of the highly sensitive test for ferric iron.

(*c*) *Study of hydrolysis.* In the hydrolysis of a salt of a weak base and a strong acid or of a weak acid and a strong base, there is an equilibrium between the salt, the free acid and the free base:

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base} \text{ (see Section } \mathbf{I, 40}\text{)}.$$

The concentration of the weak acid or of the weak base can be determined by distribution between water and another solvent, such as benzene or chloroform; the partition coefficient of the acid or base between the water and the other solvent must, of course, be known. The degree of hydrolysis may then be calculated from the concentration of the salt and the determined concentration of the weak acid or base. An example of such a salt is aniline hydrochloride. This is partially hydrolysed into aniline and hydrogen chloride. Upon shaking the aqueous solution with benzene, the aniline will distribute itself between the water and benzene in the ratio of the distribution coefficient. The initial concentration of aniline hydrochloride is known, the concentration of the free aniline in the aqueous solution can be computed from that found in the benzene solution, and from this the total concentration of aniline, produced by hydrolysis, is deduced. Sufficient data are then available for the calculation of the degree of hydrolysis.

(*d*) *The determination of the constitution of complex halide ions.* Iodine is much more soluble in an aqueous solution of potassium iodide than it is in water ; this is due to the formation of potassium tri-iodide KI_3. The following equilibrium exists in such a solution :

$$KI + I_2 \rightleftharpoons KI_3.$$

If the solution is titrated with standard sodium thiosulphate solution, the *total* concentration of the iodine, both as free I_2 and combined as KI_3, is obtained since, as soon as some iodine is removed by interaction with the thiosulphate, a fresh amount of iodine is liberated from the tri-iodide in order to maintain the equilibrium. If, however, the solution is shaken with carbon disulphide, in which iodine alone is appreciably soluble, then the iodine in the disulphide layer is in equilibrium with the *free* iodine in the solution. By determining the concentration of the iodine in the carbon disulphide solution, the concentration of the free iodine in the aqueous solution can be calculated from the known distribution coefficient, and therefrom the total concentration of the free iodine present at equilibrium. Subtracting this from the total iodine, the concentration of the combined iodine (as KI_3) is obtained ; by subtracting the latter value from the initial concentration of potassium iodide, the concentration of the free KI is deduced. The equilibrium constant :

$$K = \frac{[KI] \times [I_2]}{[KI_3]} \quad \text{or} \quad \frac{[I^-] \times [I_2]}{[I_3^-]}$$

is then computed.

A similar method has been used for the investigation of the equilibrium between bromine and bromides :

$$Br_2 + KBr \rightleftharpoons KBr_3, \text{ or } Br_2 + Br^- \rightleftharpoons Br_3^-.$$

I, 43. The Colloidal State.—It sometimes happens in qualitative analysis that a substance does not appear as a precipitate when the reactants are present in such concentrations that the solubility product of the substance is greatly exceeded and precautions are taken against supersaturation of the resulting solution. Thus when hydrogen sulpide is passed into a cooled solution of arsenious sulphide, no precipitate is discernible when one looks through the resulting mixture. The solution, however, has acquired a deep yellow colour and when viewed by reflected light shows a marked opalescence. If a powerful beam of light is passed through the solution and the latter viewed at right angles to the incident light, a scattering of light is observed, evidently due to the light reflected by the particles in suspension in the solution. This is called the **Tyndall effect.** True solutions, *i.e.*, those with particles of molecular dimensions do not exhibit a Tyndall effect, and are said to be "optically empty." Clearly the reaction has taken place forming arsenious sulphide, but the particles are in such a fine state of division that they do not appear as a precipitate. They are in fact in the **colloidal state** or in **colloidal suspension.** Other colloidal suspensions which may be encountered in qualitative analysis include ferric-, chromic- and aluminium hydroxides, cupric, manganous and nickel sulphides, silver chloride and silicic acid.

Further examination of the colloidal suspension of arsenious sulphide brings to light other peculiar properties. When an attempt is made to filter off the suspension, the particles are found to pass right through the filter paper. Also, when the colloidal suspension is allowed to stand for a long time, no appreciable settling takes place; no precipitation takes place upon shaking with solid arsenious sulphide, thus ruling out the possibility of supersaturation. The addition of, say, aluminium sulphate solution bring about immediate precipitation of arsenious sulphide, although there is no apparent reaction between the Al^{+++} or SO_4^{--} with any ion in the solution. Potassium chloride solution produces the same effect but considerably more of it must be added. Any electrolyte, in fact, causes precipitation, *i.e.*, **coagulation** or **flocculation** of the colloidal material. Heating the solution also favours coagulation. It is evident that the colloidal state must be avoided in qualitative analysis, and a more detailed account of the phenomenon will therefore be given.

The colloidal state of matter is distinguished by a certain range of particle size, as a consequence of which certain characteristic properties become apparent. Before discussing these, mention must be made of the various units which are employed in expressing small quantities. The most important of these are :—

1 micron = 1 μ = 10^{-3} mm. = 10^{-6} m.
1 milli-micron = 1 $m.\mu$ = 1 $\mu\mu$ = 10^{-6} mm.
1 Angstrom unit = 1 Å = 10^{-10} m. = 10^{-7} mm. = 0·1 $m\mu$.

Colloidal properties are, in general, exhibited by substances of particle size ranging between 0·1 μ and 1 $m\mu$. Ordinary qualitative filter paper will retain particles up to a diameter of 1–2 × 10^{-2} mm. or 10–20 μ, so that colloidal solutions in this respect behave like true solutions (the size of molecules is of the order 0·1 $m\mu$ or 10^{-8} cm.). The limit of vision under the microscope is about 0·2 μ, whilst that of the ultra-microscope is about 10 $m\mu$. Colloidal solutions are not true solutions. Close examination shows that they are not homogeneous, but consist of suspensions of solid or liquid particles in a liquid. Such a mixture is known as a **disperse system**; the liquid (usually water in qualitative analysis) is called the **dispersion medium** and the colloid the **disperse phase**.

An important consequence of the smallness of the size of the particles in a colloidal solution is that the ratio of the surface to the weight is extremely large. Phenomena which depend upon the size of the surface, such as **adsorption**, will therefore play an important part.

The characteristic properties of colloidal particles are:

(i) They exhibit a Tyndall effect when viewed with proper illumination.

(ii) They may be separated from true solutions of substances by means of a collodion or parchment membrane.

(iii) They may be regarded as possessing electrical charges since they migrate under the influence of a suitable potential gradient.

For convenience, colloids may be divided into two main groups, designated as suspensoids and emulsoids*. The chief properties of each class are summarised in the following table, although it must be emphasised that the distinction is not an absolute one, since some gelatinous precipitates (*e.g.*, aluminium and other metallic hydroxides) have properties intermediate between those of suspensoids and emulsoids.

Negative colloids include metallic sols, sulphides, silicic acid, stannic acid, silver halides, gums, starch, and certain dyes. Positive colloids include metallic hydroxides, albumin, and many dyes.

The process of dispersing a flocculated solid or gel to form a colloidal solution (or sol) is called **peptisation.**

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* For a detailed account, see A. W. Thomas, *Colloid Chemistry*, 1934 (McGraw-Hill).

Suspensoids (or Lyophobic Colloids)	*Emulsoids* (or Lyophilic Colloids)
1. The solutions (or *sols*) are only slightly viscous. Examples: sols of metals, silver halides, metallic sulphides, etc.	1. The solutions are very viscous ; they set to jelly-like masses known as *gels*. Examples : sols of silicic acid, stannic oxide, gelatin.
2. A comparatively minute concentration of an electrolyte results in flocculation. The change is, in general, irreversible ; water has no effect upon the flocculant.	2. Comparatively large concentrations of electrolytes are required to cause precipitation (" salting out "). The change is, in general, reversible, and is effected by the addition of a solvent (water).
3. Suspensoids, ordinarily, have an electric charge of definite sign, which can be changed only by special methods.	3. Most emulsoids change their charge readily, *e.g.*, they are positively charged in acid medium and negatively charged in an alkaline medium.
4. The ultra-microscope reveals bright particles in vigorous motion (Brownian movement).	4. Only a diffuse light cone is exhibited under the ultramicroscope.

The stability of a colloidal solution is intimately associated with the electrical charge on the particles. Thus in the formation of an arsenious sulphide sol by precipitation with hydrogen sulphide in faintly acid solution, sulphide ions are primarily adsorbed (since every precipitate has a tendency to adsorb its own ions), and in order to maintain the electroneutrality of the solution, an equivalent quantity of hydrogen ions is secondarily adsorbed. The hydrogen ions or other ions which are secondarily adsorbed have been termed **counter ions.** Thus the so-called electrical double layer is set up between the particles and the solution. If the electrical double layer is destroyed, the sol is no longer stable, and the particles will flocculate since the concentration is in excess of the solubility product. Thus if barium chloride solution is added, barium ions are preferentially adsorbed by the particles ; the orientation of the surface is disturbed and the charge disappears. After flocculation, it is found that the dispersion medium is acid owing to the liberation of the hydrogen counter ions. It appears that ions of opposite charge to those primarily adsorbed on the surface are necessary for coagulation. The minimum amount of electrolyte necessary to cause flocculation is called the **flocculation or coagulation value**. It has been found that the latter depends upon the valency of the ions of the opposite charge to that on the colloidal particle, the higher the valency the smaller the coagulation value; the nature of the ions has some influence also. If two sols of opposite charge are mixed (*e.g.*, ferric hydroxide and arsenious sulphide), mutual coagulation usually occurs because of the neutralisation of charges.

The above remarks apply largely to suspensoids. Emulsoids are generally very more difficult to coagulate than suspensoids. If an emulsoid sol, *e.g.*, of gelatin, is added to a suspensoid sol, *e.g.*, of gold, then the suspensoid sol appears to be strongly protected against the flocculating action of electrolytes. It is probable that the particles of the emulsoid sol are adsorbed by the suspensoid and impart their own properties to the latter. The emulsoid is known as a **protective colloid**. This explains the relative stability of the otherwise unstable gold sols produced by the addition of a little gelatin. For this reason organic matter, which might form a protective colloid, is generally destroyed before proceeding with an analysis.

During the flocculation of a colloid by an electrolyte, the ion of opposite sign to that of the colloid is adsorbed to a varying degree on the surface; the higher the valency of the ion, the more strongly is it adsorbed. In all cases, the precipitate will be contaminated by surface adsorption. Upon washing the precipitate with water, part of the adsorbed electrolyte is removed, and a new difficulty may arise. The electrolyte concentration in the supernatant liquid may fall below the coagulation value, and the precipitate will pass into colloidal solution again. This phenomenon is known as **peptisation**. It can be prevented by washing the precipitate with a suitable electrolyte.

The adsorptive properties of colloids find some application in analysis, *e.g.*, (i) in the removal of phosphates by hydrated stannic oxide in the presence of nitric acid (Section **VI, 2**, (**c**)), and (ii) in the formation of **coloured lakes** from colloidal metallic hydroxides and certain soluble dyes (see tests for Aluminium in Section **III, 21**, and for Magnesium in Section **III, 33**). There is, however, some evidence that lake formation may be partly chemical in character.

Precipitates thrown down from dilute or very concentrated solutions are often in the form of very fine crystals. These fine precipitates will generally become filterable if allowed to stand for some time in contact with the mother liquor, preferably, if the solubility permits, near the boiling point of the solution. The addition of **macerated filter paper**, in the form of a *Whatman accelerator,* is beneficial; the latter is particularly valuable for assisting the filtration of colloidal precipitates. When the precipitation has taken place from concentrated solution, the crystals are formed so rapidly that they are imperfect. On standing the crystals tend to perfect themselves: very small particles have a greater solubility than larger particles, hence they dissolve and are deposited upon the larger crystals. Occasionally the precipitate first formed is a metastable modification which is changed on standing into a more stable and less soluble state. The process of ageing of precipitates is spoken of as **digestion.**

When a precipitate separates from a solution, it is not always perfectly pure: it may contain varying amounts of impurities dependent upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed **coprecipitation**. Two important types of coprecipitation must be distinguished. The first is concerned with adsorption at the surface of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles. Surface adsorption is, in general, greatest for gelatinous precipitates and least for those of pronounced macro-crystalline character.

Some precipitates are deposited slowly and the solution is in a state of supersaturation for a considerable time. Thus, when calcium oxalate is precipitated in the presence of a high concentration of magnesium ions, the precipitate is practically pure at first, but if it is allowed to remain in contact with the solution, magnesium oxalate forms slowly and the presence of the calcium oxalate precipitate tends to accelerate the formation of the magnesium oxalate. This precipitation (magnesium oxalate) which occurs on the surface of the first precipitate (calcium oxalate) *after* its formation is termed **post-precipitation.** It generally occurs with sparingly soluble substances which form super-saturated solutions; they usually have an ion in common with the primary precipitate. Another example is the precipitation of copper or mercuric sulphide in $0{\cdot}3N$ hydrochloric acid solution in the presence of zinc ions; zinc sulphide is slowly post-precipitated.

CHAPTER II

ANALYTICAL OPERATIONS

BEFORE the student attempts to carry out the analytical reactions of the various cations and anions detailed in Chapters III and IV, he should be familiar with the operations commonly employed in qualitative analysis, that is, with the laboratory technique involved. It is assumed that the student has had some training in elementary practical chemistry, such as that given in the author's manual * ; he should be familiar with such operations as solution, evaporation, crystallisation, distillation, precipitation, filtration, decantation, bending of glass tubes, preparation of ignition tubes, boring of corks and construction of a wash bottle. These will therefore be either very briefly discussed or not described at all in the following pages.

Qualitative analysis utilises two kinds of tests, dry reactions and wet reactions. The former are applicable to solid substances and the latter to substances in solution.

II, 1. DRY REACTIONS

1. **Action of heat.** The substance is placed in a small ignition tube (bulb tube), prepared from soft glass tubing, and heated in a Bunsen flame, gently at first and then more strongly. Small test-tubes, $2\frac{1}{2}$–3 inches × $\frac{1}{4}$–$\frac{3}{8}$ inches, which are readily obtainable and are cheap, may also be employed. Sublimation may take place, or the material may melt or may decompose with an attendant change in colour, or a gas may be evolved which can be recognised by certain characteristic properties (see Chapter V, Section **V, 2**, Preliminary Dry Tests, Test i).

2. **Blowpipe tests.** A luminous Bunsen flame (air holes completely closed), about 2 inches long, is employed for these tests. A *reducing flame* is produced by placing the nozzle of a mouth blowpipe just outside the flame, and blowing gently so as to cause the *inner cone* to play on the substance under examination. An *oxidising flame* is obtained by holding the nozzle of the blowpipe about one-third within the flame and blowing somewhat more vigorously in a direction parallel with the burner top ; the extreme tip of the flame is allowed to play upon the substance.

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* *Elementary Practical Chemistry*, 1936, Blackie and Son, Ltd., London.

The tests are carried out upon a charcoal block in which a small cavity has been made with a pen-knife or with a small coin. A little of the substance is placed in the cavity and heated in the oxidising flame. Decrepitation will occur with crystalline salts ; deflagration indicates the presence of an oxidising agent (nitrate, nitrite, chlorate, *etc.*). More frequently the powdered substance is mixed with twice its bulk of anhydrous sodium carbonate or, preferably, with " fusion mixture " (an equi-molecular mixture of sodium and potassium carbonates ; this has a lower melting point than sodium carbonate alone) in the reducing flame. The initial reaction consists in the formation of the carbonates of the cations present and of the alkali salts of the anions. The alkali salts are adsorbed by the porous charcoal, and the carbonates are, for the most part, decomposed into the oxides and carbon dioxide. The oxides of the metals may further decompose, or be reduced, to the metals or they may remain unchanged. The final products of the reaction are therefore either the metals alone, metals and their oxides or oxides. The oxides of the noble metals (silver and gold) are decomposed without the aid of the charcoal into the metal, which is often obtained as a globule, and oxygen. The oxides of lead, copper, bismuth, antimony, tin, iron, nickel and cobalt are reduced either to a fused metallic globule (Pb, Bi, Sn and Sb) or to a sintered mass (Cu) or to glistening metallic fragments (Fe, Ni and Co). The oxides of cadmium, arsenic and zinc are readily reduced to the metal, but these are so volatile that they vaporise and are carried from the reducing to the oxidising zone of the flame, where they are converted into difficultly volatile oxides. The oxides thus formed are deposited as an incrustation round the cavity of the charcoal block. Zinc yields an incrustation which is yellow while hot and white when cold ; that of cadmium is brown ; that of arsenic is white and is accompanied by a garlic odour due to the volatilisation of the arsenic. A characteristic incrustation accompanies the globules of lead, bismuth and antimony.

The oxides of aluminium, calcium, strontium, barium and magnesium are not reduced by charcoal ; they are infusible and glow brightly when strongly heated. If the white residue or white incrustation left on a charcoal block is treated with a drop of cobalt nitrate solution and again heated, a bright blue colour, which probably consists of either a compound or a solid solution of cobaltous and aluminium oxides (Thenard's blue), indicates the presence of aluminium*, a pale green colour, probably of similar composition (Rinmann's green), is indicative of zinc oxide, and a pale pink mass is formed when magnesium oxide is present (see Chapter V, Section **V, 2,** Preliminary Dry Tests, Test iii).

3. **Flame tests.** In order to understand the operations involved in the flame colour tests and the various bead tests to be described subsequently, it is necessary to have some knowledge of the structure of the non-luminous Bunsen flame (Fig. 7).

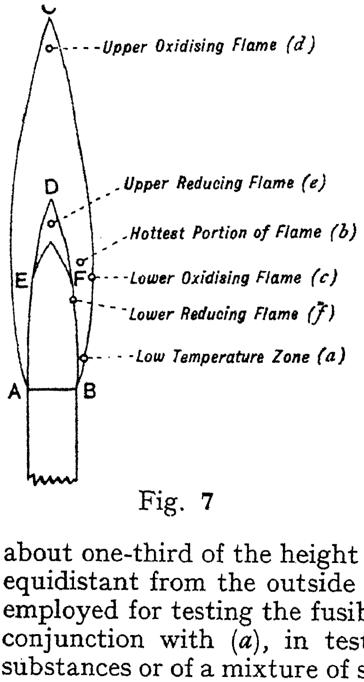
C
Upper Oxidising Flame (*d*)
D
Upper Reducing Flame (*e*)
Hottest Portion of Flame (*b*)
E
F
Lower Oxidising Flame (*c*)
Lower Reducing Flame (*f*)
Low Temperature Zone (*a*)
A
B

Fig. 7

The non-luminous Bunsen flame consists of three parts: (i) an inner blue cone *ADB* consisting largely of unburnt gas; (ii) a luminous tip at *D* (this is only visible when the air holes are slightly closed); and (iii) an outer mantle *ACBD* in which complete combustion of the gas occurs. The principal parts of the flame, according to Bunsen, are clearly indicated in Fig. 7. The lowest temperature is at the base of the flame (*a*); this is employed for testing volatile substances to determine whether they impart any colour to the flame. The hottest part of the flame is the fusion zone at (*b*) and lies at about one-third of the height of the flame and approximately equidistant from the outside and inside of the mantle; it is employed for testing the fusibility of substances, and also, in conjunction with (*a*), in testing the relative volatilities of substances or of a mixture of substances. The *lower oxidising zone* (*c*) is situated on the outer border of (*b*) and is used for the oxidation of substances dissolved in beads of borax, sodium carbonate or microcosmic salt. The *upper oxidising zone* (*d*) consists of the non-luminous tip of the flame; here a large excess of oxygen is present and the flame is not so hot as at (*c*). It is used for all oxidation processes in which the highest temperature is not required. The ***upper reducing flame*** (*e*) is at the tip of the inner blue zone and is rich in incandescent carbon; it is especially useful for reducing oxide incrustations to the metal. The ***lower reducing zone*** (*f*) is situated in the inner edge of the mantle next to the blue cone and it is here that the reducing gases mix with the oxygen of the air; it is a less powerful reducing zone than (*e*), and is employed for the reduction of fused borax and similar beads.

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* A blue colour is also given by phosphates, arsenates, silicates or borates.

We can now return to the flame tests. Compounds of certain metals are volatilised in the non-luminous Bunsen flame and impart characteristic colours to the flame. The chlorides are amongst the most volatile compounds, and these are prepared ***in situ*** by mixing the compound with a little concentrated hydrochloric acid before carrying out the tests. The procedure is as follows. A thin platinum wire about 5 cms. long, fused into the end of a short piece of glass tubing or glass rod which serves as a handle, is employed. This is first thoroughly cleaned by dipping it into concentrated hydrochloric acid contained in a watch glass and then heating it in the fusion zone (*b*) of the Bunsen flame; the wire is clean when it imparts no colour to the flame. The wire is dipped into concentrated hydrochloric acid on a watch glass, then into a little of the substance whereby a little adheres to the wire. It is then introduced into the lower oxidising flame (*c*), and the colour imparted to the flame observed. Less volatile substances are heated in the fusion zone (*b*); in this way it is possible to make use of the difference in volatilities for the separation of the constituents of a mixture.

A table showing the colours imparted to the flame by salts of different metals is given in Chapter V, Section **V, 2,** Preliminary Dry Tests ii. Carry out flame tests with the chlorides of sodium, potassium, calcium, strontium and barium and record the colours you observe. Repeat the test with a mixture of sodium and potassium chlorides. The yellow colouration due to the sodium masks that of the potassium. View the flame through two thicknesses of cobalt glass; the yellow sodium colour is absorbed and the potassium flame appears crimson.

Potassium chloride is much more volatile than the chlorides of the alkaline earth metals. It is therefore possible to detect potassium in the lower oxidising flame and the calcium, strontium and barium in the fusion zone.

After all the tests, the platinum wire should be cleaned with concentrated hydrochloric acid. It is a good plan to store the wire permanently in the acid. A cork is selected that just fits into a test-tube, and a hole bored through the cork through which the glass holder of the platinum wire is passed. The test-tube is about half filled with concentrated hydrochloric acid so that when the cork is placed in position, the platinum wire is immersed in the acid.

A platinum wire sometimes acquires a deposit which is removed with difficulty by hydrochloric acid and heat. It is then best to employ fused potassium hydrogen sulphate. A coating of potassium hydrogen sulphate is made to adhere to the wire by drawing the hot wire across a piece of the solid salt. Upon passing the wire slowly through a flame, the bead of potassium pyrosulphate which forms travels along the wire, dissolving the contaminating deposits. When cool, the bead is readily dislodged. Any small residue of pyrosulphate dissolves at once in water, whilst the last traces are usually removed by a single moistening with concentrated hydrochloric acid, followed by heating. The resulting bright clean platinum wire imparts no colour to the flame.

4. **Spectroscopic tests. Flame spectra.** The only trustworthy way to employ flame tests in analysis is to resolve the light into its component tints and to identify the cations present by their characteristic sets of tints. The instrument employed to resolve light into its component colours is called a **spectroscope.** A simple form is shown in Fig. 8. It consists

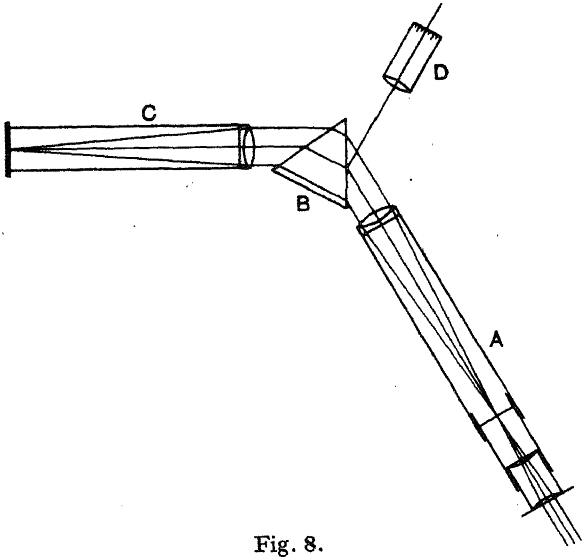

Fig. 8.

of a collimator *A* which throws a beam of parallel rays on the prism *B*, mounted on a turn-table ; the telescope *C* through which the spectrum is observed ; and a tube *D*, which contains a scale of reference lines which may be superposed upon the spectrum. The spectroscope is calibrated by observing the spectra of known substances, such as sodium chloride, potassium chloride, thallium chloride and lithium chloride. The conspicuous lines are located on a graph drawn with wave-lengths as ordinates and scale divisions as abscissae. The wave-length curve may then be employed in obtaining the wave-lengths of all intermediate positions and also in establishing the identity of the component elements of a mixture.

To adjust the simple table spectroscope described above (which is always mounted on a rigid stand) a lighted Bunsen burner is placed in front of the collimator *A* at a distance of about 10 cm. from the slit. Some sodium chloride is introduced by means of a clean platinum wire into the lower part of the flame, and the tube containing the adjustable slit rotated until the sodium line, as seen through the telescope *C*, is in a vertical position. The sodium line is then sharply focussed by suitably adjusting the sliding tubes of the collimator and the telescope. Finally, the scale *D* is illuminated by placing a small electric lamp in front of it, and the scale sharply focussed. The slit should also be made narrow in order that the position of the lines on the scale can be accurately noted.

A smaller and more compact instrument, which is more useful for routine tests in qualitative analysis, is the **direct vision spectroscope**, shown in Fig. 9. The instrument is adjusted

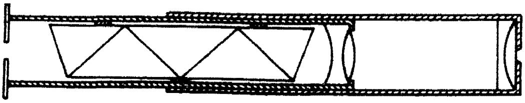

Fig. 9.

by directing it towards the sun, adjusting the slit and focussing the tube until the sunlight spectrum (Fraunhofer lines) appear sharply defined.

If a sodium compound is introduced into the colourless Bunsen flame, it colours it yellow ; if the light is examined by means of a spectroscope, a bright yellow line is visible. By narrowing the slit, two fine yellow lines may be seen. The mean wave-length corresponding to these two lines is 5893×10^{-7} mm. Wave-lengths are generally expressed in Angstrom units; one Angstrom unit (or 1 Å) = 10^{-7} mm. = 10^{-10} m.; sometimes the unit $\mu\mu$ or $m\mu$ (milli-micron) is employed to express 10^{-6} mm. or 10^{-9} m. The mean wave-length of the two sodium lines is therefore 5893 Å or 589·3 $m\mu$. The elements which are usually identified by the spectroscope in qualitative analysis are :—sodium, potassium, lithium, thallium, and less frequently, because of the comparative complexity of their spectra, calcium, strontium and barium. The wave-lengths of the brightest lines, visible through a good-quality direct vision spectroscope, are collected in the following table. As already stated, the spectra of the alkaline earth metals are relatively complex and consist of a number of fine lines ; the wave-lengths of the brightest of these are given. If the resolution of the spectroscope is small, they will appear as bands.

Element	*Description of Line*	*Wave-length in Å*
Sodium	Double yellow	5890, 5896
Potassium	Double red	7665, 7669
	Double violet	4044, 4047
Lithium	Red	6708
	Faint orange-yellow	6103
Thallium	Green	5351
Calcium	Red	6162
	Green	5590
	Violet	4227
Strontium	Red	6870
	Orange	6060
	Blue	4607
	Violet	4078
Barium	Green	5778, 5536, 5519, 5425, 5137
	Blue	4874

The spectra of the various elements are shown diagrammatically in Fig. 10 ; the position of the lines have been drawn to scale.

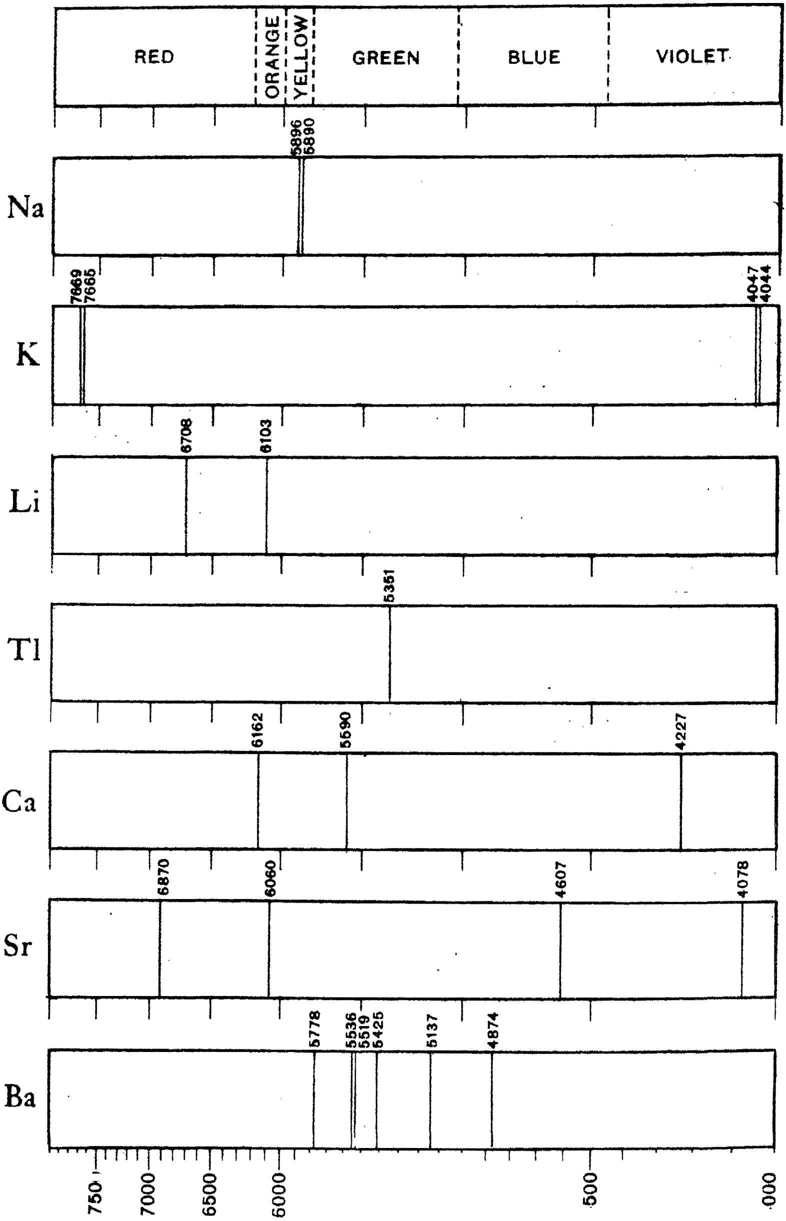
RED
ORANGE
YELLOW
GREEN
BLUE
VIOLET
Na
5896
5890
K
7669
7665
4047
4044
Li
6708
6103
Tl
5351
Ca
6162
5590
4227
Sr
6870
6060
4607
4078
Ba
5778
5536
5519
5425
5137
4874
750
7000
6500
6000
500
000

Fig. 10.

A more extended discussion is outside the scope of this volume, and the reader is referred to the standard works on the subject*.

5 **Borax bead tests.** A platinum wire, similar to that referred to under flame tests, is used for the borax bead tests. The free end of the platinum wire is coiled into a small loop through which an ordinary match will barely pass. The loop is heated in the Bunsen flame until it is red hot and then quickly dipped into powdered borax $Na_2B_4O_7,10H_2O$. The adhering solid is held in the hottest part of the flame ; the salt swells up as it loses its water of crystallisation and shrinks upon the loop forming a colourless, transparent, glass-like bead consisting of a mixture of sodium metaborate and boric anhydride : ‡

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3.$$

The bead is moistened (this may be done with the tongue) and dipped into the finely powdered substance whereby only a minute amount of the substance will adhere to the bead. It is important to employ a minute amount of substance as otherwise the bead will become dark and opaque in the subsequent heating. The bead and adhering substance is heated first in the lower reducing flame, allowed to cool and the colour observed. It is then heated in the lower oxidising flame, allowed to cool and the colour observed again.

Characteristic coloured beads are produced with salts of copper, iron, chromium, manganese, cobalt and nickel. The student should carry out borax bead tests with salts of these metals and compare his results with those tabulated in Chapter V, Section **V, 2,** Preliminary Dry Tests, iv.

After each test, the bead is removed from the wire by heating it again to fusion, and then jerking it off the wire into a vessel of water. The borax bead also provides an excellent method for cleaning a platinum wire ; a borax bead is run backwards and forwards along the wire by suitably heating, and is then shaken off by a sudden jerk.

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* See, for example, W. A. Brodie, *Chemical Spectroscopy*, 1939 (J. Wiley ; Chapman and Hall).

‡ Some authors, notably Treadwell, do not recommend the use of a loop on the platinum wire as it is considered that too large a surface of the platinum is thereby exposed. According to their procedure, the alternate dipping into borax and heating is repeated until a bead 1·5–2 mm. in diameter is obtained. The danger of the bead falling off is reduced by holding the wire horizontally. It is the present author's experience that the loop method is far more satisfactory, especially in the hands of beginners, and is less time-consuming.

The coloured borax beads are due to the formation of coloured borates; in those cases where different coloured beads are obtained in the oxidising and the reducing flames, borates corresponding to varying stages of oxidation of the metal are produced. Thus with copper salts in the oxidising flame, one has:

$$Na_2B_4O_7 = 2NaBO_2{,}B_2O_3\,;$$
$$CuO + B_2O_3 = Cu(BO_2)_2 \text{ (cupric metaborate).}$$

The reaction:

$$CuO + NaBO_2 = NaCuBO_3 \text{ (orthoborate),}$$

probably also occurs. In the reducing flame (*i.e.*, in the presence of carbon), two reactions may occur: (i) the coloured cupric salt is reduced to colourless cuprous metaborate—

$$2Cu(BO_2)_2 + 4NaBO_2 + C = Cu_2(BO_2)_2 + Na_2B_4O_7 + CO\,;$$

(ii) the cupric borate is reduced to metallic copper, so that the bead appears red and opaque—

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C = 2Cu + 2Na_2B_4O_7 + 2CO.$$

With iron salts $Fe(BO_2)_2$ and $Fe(BO_2)_3$ are formed in the reducing and oxidising flames respectively.

Some authors assume that the metal metaborate may combine with sodium metaborate to give complex borates of the type $Na_2[Cu(BO_2)_4]$, $Na_2[Ni(BO_2)_4]$ and $Na_2[Co(BO_2)_4]$:

$$Cu(BO_2)_2 + 2NaBO_2 = Na_2[Cu(BO_2)_4].$$

6. **Phosphate or microcosmic salt bead tests.** The bead is produced similarly to the borax bead except that microcosmic salt, $Na(NH_4)HPO_4{,}4H_2O$, is used. The colourless, transparent bead contains sodium metaphosphate:

$$Na(NH_4)HPO_4 = NaPO_3 + H_2O + NH_3.$$

This combines with metallic oxides forming orthophosphates, which are often coloured. Thus a blue phosphate bead is obtained with cobalt salts:

$$NaPO_3 + CoO = NaCoPO_4.$$

The sodium metaphosphate glass exhibits little tendency to combine with acidic oxides. Silica, in particular, is not dissolved by the phosphate bead. When a silicate is strongly heated in the bead, silica is liberated and this remains suspended in the bead in the form of a semi-translucent mass; the so-called silica " skeleton " is seen in the bead during and after fusion. This reaction is employed for the detection of silicates:

$$CaSiO_3 + NaPO_3 = NaCaPO_4 + SiO_2.$$

It must, however, be pointed out that many silicates dissolve completely in the bead so that the absence of a silica "skeleton" does not conclusively prove that a silicate is not present.

In general, it may be stated that the borax beads are more viscous than the phosphate beads. They accordingly adhere better to the platinum wire loop. The colours of the phosphates, which are generally similar to those of the borax beads, are usually more pronounced. The various colours of the phosphate beads are collected in the following table.

Oxidising Flame	*Reducing Flame*	*Metal*
Green when hot, blue when cold.	Colourless when hot, red when cold.	**Copper**
Yellowish- or reddish-brown when hot, yellow when cold.	Yellow when hot, colourless when cold.	**Iron**
Green, hot and cold.	Green, hot and cold.	**Chromium**
Violet, hot and cold.	Colourless, hot and cold.	**Manganese**
Blue, hot and cold.	Blue, hot and cold.	**Cobalt**
Brown, hot and cold.	Grey when cold.	**Nickel**

7. **Sodium carbonate bead tests.** The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame; a white, opaque bead is produced. If this is moistened, dipped into a little potassium nitrate and then into a small quantity of a manganese compound, and the whole heated in the oxidising flame, a *green* bead of sodium manganate is formed:

$$MnO + Na_2CO_3 + O_2 = Na_2MnO_4 + CO_2.$$

A *yellow* bead is obtained with chromium compounds, due to the production of sodium chromate:

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2.$$

II, 2. WET REACTIONS

These tests are made with substances in solution. A reaction is known to take place (*a*) by the formation of a precipitate, (*b*) by the evolution of a gas or (*c*) by a change of colour. The major number of the reactions of qualitative analysis are carried out in the wet way and details of these are given in later chapters. The following notes upon the methods to be adopted in carrying out the tests will be found of value and should be carefully studied.

Test-tubes. The best size for general use is 6 inches × ⅝ inch. It is useful to remember that 10 c.c. of liquid fills a test-tube of this size to a depth of about 1½ inches. Smaller test-tubes are sometimes used for special tests. For heating moderate volumes of liquids a somewhat larger tube, about 7 inches × 1 inch, the so-called " boiling tube," is recommended. A test-tube brush should be available for cleaning the tubes.

Beakers. Those of 50, 100 and 250 c.c. capacity and of the Griffin form are the most useful in qualitative analysis. Clock glasses of the appropriate size should be provided. For evaporations and chemical reactions which are likely to become vigorous, the clock glass should be supported on the rim of the beaker by means of V-shaped glass rods.

Conical or Erlenmeyer flasks. These should be of 100 and 250 c.c. capacity, and are useful for decompositions and evaporations. The introduction of a funnel, whose stem has been cut off, prevents loss of liquid through the neck of the flask and permits the escape of steam.

Stirring rods. A length of glass rod, of about 4 mms. diameter, is cut off into suitable lengths and the ends rounded in the Bunsen flame. The rods should be about 20 cms. long for use with test-tubes and 8–10 cms. long for work with basins and small beakers. Open glass tubes must not be used as stirring rods. A rod pointed at one end, prepared by heating a glass rod in the flame, drawing it out when soft as in the preparation of a glass jet and then cutting it into two, is employed for piercing the apex of a filter paper to enable one to transfer the contents of a filter paper by means of a stream of water from a wash-bottle into another vessel.

A rubber-tipped glass rod or " policeman " is employed for removing any solid from the sides of glass vessels.

Wash-bottle. This should consist of a 500 c.c. flat-bottomed flask, and the stopper carrying the two tubes should preferably be of rubber. It is recommended that the wash-bottle be kept ready for use filled with hot water as it is usual to wash precipitates with hot water; this runs through the filter paper rapidly and has a greater solvent power than cold water, so that less is required for efficient washing. Asbestos string or cloth should be wound round the neck of the flask in order to protect the hand.

Precipitation. When excess of a reagent is to be used in the formation of a precipitate, this does not mean that an excessive amount of it should be employed. In most cases, unless specifically stated, only a moderate amount over that required to bring about the reaction is necessary. This is usually best detected by filtering a little of the mixture and testing the filtrate with the reagent; if no further precipitation occurs, a sufficient excess of the reagent has been added.

Precipitation with hydrogen sulphide. This operation is of such importance in qualitative analysis that it merits a detailed discussion. One method which is employed consists in passing a stream of the gas in the form of bubbles through the solution contained in an open test-tube or beaker (Fig. 11, *a*); this procedure is termed the "bubbling" method. The efficiency of this method is low; absorption of the gas takes place at the surface of the bubbles, and, since the gas is absorbed slowly, most of it escapes into the air of the fume-chamber. Another method (the "pressure" method) is best described with the aid of Fig. 11, *b*. The solution is contained in a small conical flask provided with a stopper and lead-in tube. The stopper is first loosened in the neck of the flask, and the gas stream turned on so as to displace most of the air from the flask. After a very short time the stopper is inserted tightly and the flask shaken from time to time. The

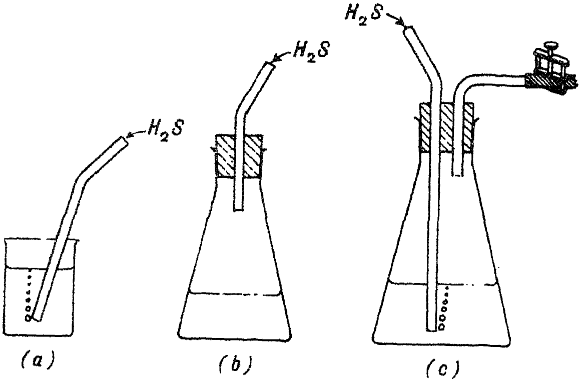

Fig. 11.

advantages of this method are: (i) a large surface of the liquid is presented to the gas and (ii) it prevents the escape of large amounts of unused gas. The only merit of the "bubbling" method is that the bubbles keep the solution stirred. The advantages of both methods are incorporated in the apparatus of Fig. 11, *c*. Here the hydrogen sulphide is allowed to bubble freely until most of the air is expelled from the flask, and then the exit tube, carrying a short length of thick-walled rubber tubing is closed by a screw clip (as in the Figure) or by a tightly-fitting short length of glass rod (alternatively, a glass stop-cock may be used). As absorption proceeds, gas bubbles through the solution, thereby keeping it stirred; it is advisable, however, to shake the flask from time to time. It need hardly be stated that precautions for "sucking back" should be taken, and that the delivery tube must be thoroughly cleaned after each precipitation.

Filtration. The purpose of filtration is, of course, to separate the mother liquor and excess of reagent from the precipitate. A moderately fine-textured filter paper is generally employed. The size of the filter paper is controlled by the quantity of precipitate and not by the volume of the solution. The upper edge of the filter paper should be about 1 cm. from the upper rim of the glass funnel. It should never be more than about two-thirds full of the precipitate. Liquids containing precipitates should be heated before filtration except in special cases, such as those containing lead chloride which is more soluble in hot than cold water. Gelatinous precipitates, which often clog the pores of the filter paper and thus considerably reduce the rate of filtration, are best filtered through fluted filter paper, particularly in those cases, as for basic ferric acetate (Section **III, 20,** reaction *8*), where the precipitate is to be discarded. An alternative method is to add a little paper pulp to the solution containing the gelatinous precipitate and then to filter in the normal manner. When precipitates tend to pass through the filter paper, it is often a good plan to add an ammonium salt, such as ammonium chloride or nitrate, to the solution; this will prevent the formation of colloidal solutions.

A precipitate may be *washed* by decantation, as much as possible being retained in the vessel during the first two or three washings, and the precipitate then transferred to the filter paper. This procedure is unnecessary for coarse, crystalline, easy filterable precipitates as the washing can be carried out directly on the filter paper. This is best done by directing a stream of water from a wash-bottle first around the upper rim of the filter and following this down in a spiral towards the precipitate in the apex ; the filter is filled about one-half to two-thirds full at each washing. The completion of washing, *i.e.*, the removal of the precipitating agent, is tested for by chemical means ; thus if a chloride is to be removed, with silver nitrate solution. If the solution is to be tested for acidity or alkalinity, a drop of the thoroughly stirred solution, removed upon the end of a glass rod, is placed in contact with a piece of " neutral " litmus paper on a watch glass. A red colour indicates an acid and a blue colour an alkaline reaction. Other test papers are similarly employed.

Removal of the precipitate from the filter. If the precipitate is bulky, sufficient for examination can be removed with the aid of a small nickel or horn spatula. If the amount of precipitate is small, one of two methods may be employed. In the first, a small hole is pierced in the base of the filter paper with a pointed glass rod and the precipitate washed into a test-tube or a small beaker with a stream of water from the wash-bottle. In the second, the filter paper is removed from the funnel, opened out on a clock glass and scraped with a spatula.

It is frequently necessary to dissolve a precipitate completely. This is most readily done by pouring the solvent, preferably whilst hot, on to the filter and repeating the process, if necessary, until all the precipitate has passed into solution. When only a small quantity of the precipitate is available, the filter paper and precipitate may be heated with the solvent and filtered.

Aids to filtration. The simplest device is to use a funnel with a long stem, or better to attach a narrow-bored glass tube, about 18 inches long and bent as shown in Fig. 12, to the funnel by means of rubber tubing. The lower end of the tube or of the funnel should touch the side of the vessel in which the filtrate is being collected in order to avoid splashing. The velocity of filtration depends upon the length of the water column.

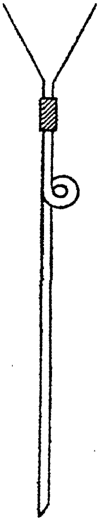

Fig. 12.

Where large quantities of liquids and/or of precipitates are to be handled, or if rapid filtration is desired, filtration with the aid of a water pump is employed. A filter flask of about 500 c.c. capacity is provided with a two-holed rubber bung, a long tube connected to the pump is passed through one hole and a short glass tap through the other hole. The side arm of the flask is connected by means of thick-walled rubber tubing, " pressure tubing," to another filter flask, the mouth of which carries a rubber bung through which a glass funnel passes. Filtration may be carried out in the usual manner under the partial vacuum created by the pump, the tap *T* (Fig. 13) being closed. The tap is opened, air thereby entering the apparatus which thus attains atmospheric pressure, as soon as the level of the liquid is about 0·5 cm. above the apex of the funnel; if this is not done, the filter paper may be sucked through into the flask. The latter difficulty is surmounted by the use of a small perforated platinum cone into which the apex of the filter paper is fitted. An alternative procedure, which obviates the use of a platinum cone, con-

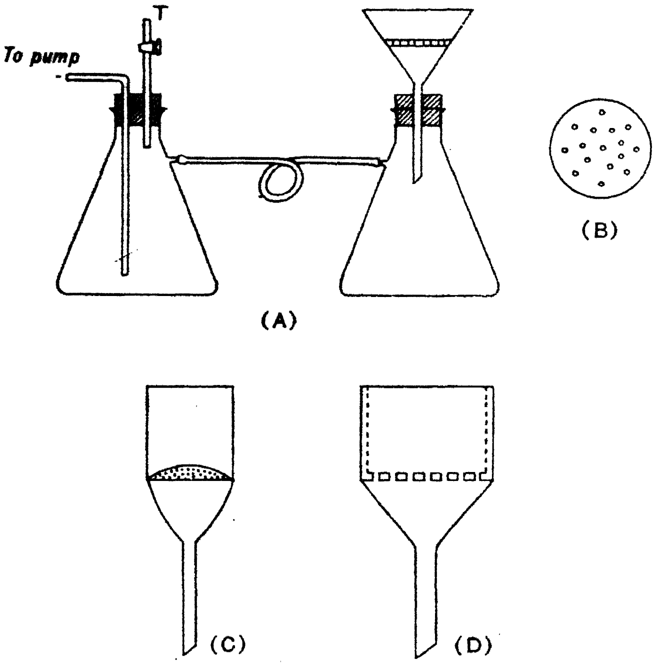

Fig. 13

sists in employing a circular piece of coarse muslin about 2 cms. in diameter. This is folded with the filter paper in the usual way and the double filter so formed is introduced into the funnel. A new muslin filter must, of course, be employed for each filtration.

A simpler method necessitates the use of a small perforated porcelain plate (*B* in Fig. 13); this is placed in the funnel and covered with two thicknesses of well-fitting filter paper, cut to the size of the plate.

For large quantities of precipitates, a small Buchner funnel (*D* in Fig.13) is employed. This consists of a porcelain funnel in which a perforated plate is incorporated. Two thicknesses of well-fitting filter paper cover the plate. The Buchner funnel is fitted by means of a cork into the filter flask. When the volume of filtrate is small, it may be collected in a small test-tube placed inside the filter flask.

Strongly acid or alkaline solutions cannot be filtered through ordinary filter paper. They may be filtered through a small pad of glass wool or asbestos placed in the apex of a glass funnel. A more convenient method is to employ a Jena glass sintered funnel; in this, a filter plate, which is available in various degrees of porosity according to the nature of the precipitate, is actually fused into a Jena glass funnel (*C* in Fig. 13). Filtration is carried out exactly as with a Buchner funnel.

Drying of precipitates. Partial drying, which is sufficient for many purposes, is accomplished by opening out the filter, laying it upon several dry filter papers and allowing them to absorb the water. More complete drying is obtained by placing the funnel containing the filter paper in a " drying cone " (a hollow tinned-iron cone or cylinder), which rests either upon a sand bath or upon a wire gauze and is heated by means of a small flame. The funnel is thus exposed to a current of hot air, which rapidly dries the filter and precipitate. Great care must be taken not to char the filter paper. A safer but slower method is to place the funnel and filter paper, or the filter paper alone resting upon a clock glass, inside a steam oven.

Cleaning of apparatus. The importance of using clean apparatus cannot be too strongly stressed. All glass-ware should be put away clean. A few minutes should be devoted at the end of the day's work to " cleaning up " ; the student should remember that wet dirt is very much easier to remove than dry dirt. A test-tube brush is provided to clean test-tubes and other glass apparatus. Test-tubes may be inverted in the test-tube stand and allowed to drain. Other apparatus, after rinsing with distilled water, should be wiped dry with a "glass cloth," that is, a cloth which has been washed at least once and contains no dressing.

Glass apparatus which appears to be particularly dirty or greasy is cleaned by soaking in "chromic acid mixture" (concentrated sulphuric acid in which potassium dichromate is dissolved), followed by a liberal washing with tap water, and then with distilled water.

Some working hints. (1) Always work in a tidy, systematic manner. Remember a tidy bench is indicative of a methodical mind. A string duster is useful to wipe up liquids spilt upon the bench. All glass and porcelain apparatus must be scrupulously clean.

(2) Reagent bottles and their stoppers should not be put upon the bench. They should be returned to their correct places upon the shelves immediately after use. If a reagent bottle is empty, it should be returned to the store-room for filling.

(3) When carrying out a test which depends upon the formation of a precipitate, make sure that both the solution to be tested and the reagent is absolutely free from suspended particles. If this is not the case, filter the solutions first.

(4) Do not waste gas or chemicals. The size of the Bunsen flame should be no larger than is absolutely necessary. It should be extinguished when no longer required. Avoid using unnecessary excess of reagents. Reagents should always be added portion-wise.

(5) Pay particular attention to the disposal of waste. Neither strong acids nor strong alkalis should be thrown into the sink; they must be largely diluted first, and the sink flushed with much water. Solids (corks, filter paper, etc.) should be placed in the special boxes provided for them in the laboratory. On no account may they be thrown into the sink.

(6) All operations involving (*a*) the passage of hydrogen sulphide into a solution, (*b*) the evaporation of concentrated acids, (*c*) the evaporation of solutions for the removal of ammonium salts and (*d*) the evolution of poisonous or disagreeable vapours or gases must be conducted in the fume chamber.

(7) All results, whether positive, negative or inconclusive, must be recorded neatly in a notebook at the *time they are*

made. The writing up of experiments should not be postponed until after the student has left the laboratory. Apart from inaccuracies which may thus creep in, the habit of performing experiments and recording them immediately is one that should be developed from the very outset.

(8) If the analysis is incomplete at the end of the laboratory period, label all solutions and precipitates clearly. It is a good plan to cover these with filter paper to prevent the entrance of dust, etc.

(9) When in difficulty, consult the teacher.

II, 3. MICRO ANALYSIS

In contrast to ordinary or macro analysis, micro analysis is concerned with the analysis of very much smaller samples with all operations carried out on a correspondingly smaller scale. Thus in macro qualitative analysis it is usual to employ up to 1 g. of the mixture and to detect all constituents present in amounts greater than 1 to 5 mg. or 0·1 to 0·5 per cent.; the concentrations of the ions are of the order of 1 to 30 mg. per c.c. The actual test which serves to detect the presence of a radical or element must be sufficiently sensitive to permit its detection in the lowest concentration, the sensitivity being dependent upon the ratio of the total volume to the weight of the radical. Thus the ordinary test for lead ions with potassium chromate solution will detect 1 mg. of lead in a total volume of 5 c.c. Provided that this ratio is maintained, it is possible to reduce the amount of lead without any appreciable loss of sensitivity, *e.g.*, if the test be carried out in a total volume of 0·1 c.c., then 0·02 mg. of lead may be detected. The only limitations are our ability to manipulate smaller volumes of liquids and to definitely identify the correspondingly smaller precipitate of lead chromate. Likewise, the systematic separations would be equally satisfactory if carried out with a smaller sample provided the ratio of the weight of the sample to the volume is kept the same. However, many of the mechanical operations of ordinary qualitative analysis are unsatisfactory or inapplicable on the reduced scale so that a special micro technique must be adopted. Moreover, as the size of the sample employed is reduced, the precipitates obtained must of necessity become smaller and smaller and a limit will ultimately be reached beyond which the naked eye cannot definitely see and recognise the precipitates. This difficulty is surmounted by the use of a microscope in examining the final precipitate, and the technique of microscope analysis has been so well developed as to permit the use of a sample weighing as little as 1 mg. A discussion of the highly specialised technique involved is outside the scope of this volume * and we shall confine our attention to those micro methods which require comparatively simple apparatus and technique. In order to avoid the use of the microscope samples should, as a general rule, weigh 5 to 10 mg. This means that in adapting, as far as possible, the procedures of macro analysis all weights and volumes must be reduced by a factor of about 0·01 ; the total amounts of each of the ions are of the order of 0·01 to 3 mg.

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* See, however, E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. I (1938), Vol. II (1930) (J. Wiley; Chapman and Hall); also A. A. Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis* (1942) (J. Wiley; Chapman and Hall).

There is another system of analysis, termed **semimicro analysis,** in which the total amounts of material involved are intermediate between those used for macro analysis and micro analysis respectively. The amounts of material dealt with in semimicro analysis are about one twentieth to one-tenth of those usually employed in macro analysis ; the total quantities of each of the ions are of the order of 0·1 to 30 mg. All weights and volumes must be reduced by a factor of 0·05 to 0·1 and, in the main, the procedures to be described for micro analysis are applicable with, of course, obvious modifications. The experimental technique for semimicro qualitative analysis, like that of micro analysis, is centred round the centrifuge, but recently H. H. Barber (1940) has introduced a simplified technique, which dispenses with the use of the centrifuge. The whole subject is discussed in detail in Chapter IX. It must be pointed out that there is no sharp line of demarcation between micro and semimicro qualitative analysis. This is in contrast to quantitative analysis ; here micro quantitative analysis, concerned with quantities of the order of a few milligrams, utilises a micro-balance (Oertling, Ainsworth FD, Kuhlmann, Bunge, etc.) weighing to 0·001 mg., whilst for semimicro analysis, dealing with quantities of the order of 0·02 to 0·04 g., an ordinary good analytical balance and the method of swings may be used for weighing to 0·01 mg.

Fortunately the small amounts of material obtained after the usual systematic separations can, in many cases, be detected by what is commonly called **spot analysis,** *i.e.*, analysis which involves the use of spots (about 0·05 c.c. or smaller) of solutions or a fraction of a milligram of solids. Spot analysis has been developed as a result of the researches of numerous chemists ; the names of Tananiev, Gutzeit, van Nieuwenburg and, particularly, Feigl and their collaborators must be mentioned in this connexion. In general, spot reactions are preferable to tests which depend upon the formation and recognition of crystals under the microscope, in that they are quicker and easier to carry out, less susceptible to experimental conditions, and much easier to interpret. It is true that incomplete schemes of qualitative analysis have been proposed,* which are based largely on spot tests, but these cannot be regarded as entirely satisfactory for very few spot tests are specific for particular ions and the adoption of such schemes will not, in the long run, help in the development of micro qualitative analysis.

* See Appendix, Section *A*, 7.

It seems to the writer that the greatest potential progress lies in the use of the ordinary macro procedures (or simple modifications of them) to effect the preliminary separations for which the specialised micro technique is adopted, followed by the utilisation of spot tests as confirmatory tests *after* the group or other separations have been carried out. Hence the following pages will contain an account of the methods for carrying out macro procedures on a micro scale and also a discussion of the technique of spot analysis.

The advantages of micro methods are :—

(i) they are more rapid than macro procedures and at least as accurate ;

(ii) the apparatus required occupies comparatively little space; and

(iii) a considerable saving of reagents is effected.

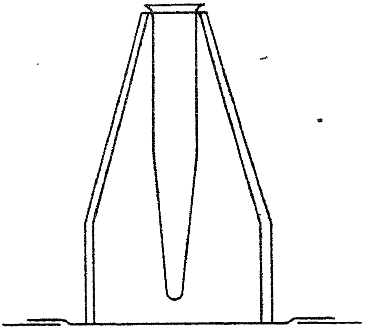
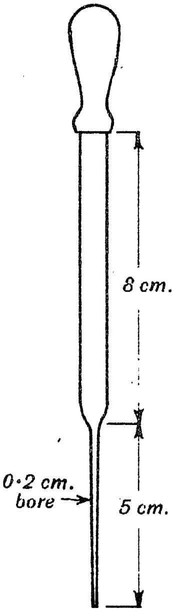


Fig. 14.
Two thirds actual size.

II, 4. Technique of Micro-qualitative Analysis.

Micro-centrifuge tubes of 0·5 to 2 c.c. capacity replace beakers, test-tubes and flasks for most operations. Such a centrifuge tube is shown in Fig. 14, together with the glass support used during heating or evaporation on a water bath. Centrifuge tubes are conveniently supported on a rack consisting of a wooden block provided with 6 to 12 holes, evenly spaced, of ⅝″ diameter and ½″ deep. **Solutions are separated from precipitates** by centrifuging instead of filtering. **Micro-centrifuges** are now available commercially ; one that is electrically driven (operating at 1500–3000 r.p.m.) is preferable to a hand-operated centrifuge. The centrifuge should be provided with a metal shield and cover to protect the operator against personal injury. In order to avoid dangerous vibration of the instrument when in use, the side of the centrifuge containing the sample tube should always be counterbalanced by a similar tube containing an equal weight of water placed on the opposite side, or it may be balanced with another tube of material to be centrifuged containing an approximately equal volume of liquid. The cover of the centrifuge must not be removed until the instrument has come to rest.

Precipitations are usually carried out in conical micro-centrifuge tubes. After centrifuging, the precipitate collects at the bottom of the tube. For centrifuge tubes to about 2 c.c. capacity a **dropper pipette** may be employed to remove the supernatant liquid from the tube ; it cannot be removed by pouring because when this is attempted a large proportion of the



ig. 15.

liquid remains in the tube. Such a dropper pipette may be readily constructed from glass tubing; the dimensions are given in Fig. 15. Another method for removing the mother liquor or centrifugate, which is particularly useful for smaller tubes (0.5 to 2 c.c. capacity), is to employ a **transfer capillary pipette**. This consists of glass tubing having an internal diameter of about 2 mm. (which may be drawn from wider tubing), 20 to 25 cm. in length with one end drawn out in a micro-flame to a tip with a fine opening. The correct method of transferring the liquid to the capillary pipette will be evident from Fig. 16. The centrifuge cone is held in the left hand and the capillary pipette is pushed slowly towards the precipitate so that the point of the capillary remains just below the surface of the liquid. As the liquid rises in the pipette, the latter is gradually lowered, always keeping the tip just below the surface of the liquid until the entire solution is in the pipette and the tip is about 1 mm. above the precipitate. The pipette is removed and the liquid blown or drained out into a clean dry centrifuge tube.

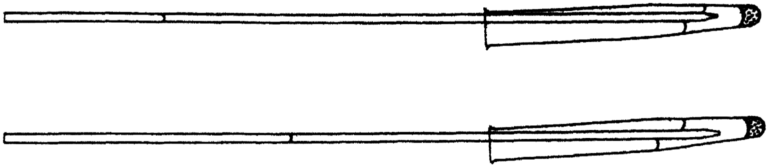


Fig. 16.

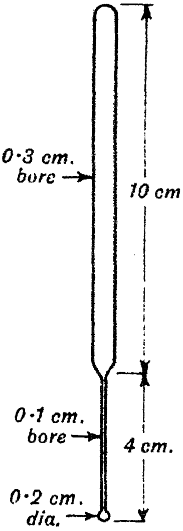


Fig. 17.

For the **washing of precipitates** the solution is added directly to the precipitate in the centrifuge tube and stirred thoroughly either by a platinum wire or by means of a stirrer, such as is shown in Fig. 17; the latter can readily be constructed from glass rod. The mixture is then centrifuged and the clear solution removed by a pipette as already described. It may be necessary to repeat this operation two or three times in order to ensure complete washing.

The **transfer of precipitates** is comparatively rare in micro-qualitative analysis. Most of the operations are usually so designed that it is only necessary to transfer solutions. However, if this should be necessary and the precipitate is crystalline, the latter may be readily sucked up by a dropper pipette and transferred. If the precipitate is gelatinous, it may be transferred

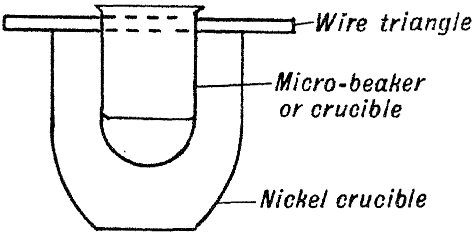


Fig. 18.

by means of a narrow glass, nickel, monel metal or platinum spatula*.

The **heating of solutions** in a centrifuge tube is best carried out by placing the latter on its glass support (see Fig. 14) and immersing in a water bath. When higher temperatures are required, as for evaporation, the liquid is transferred to a micro-beaker or crucible; this is supported by means of a copper wire triangle on a small nickel crucible as shown in Fig. 18. Heating is effected with a micro-burner or on a hot plate. Micro-beakers may be heated by means of the device shown in Fig. 19, which is laid on a water bath.

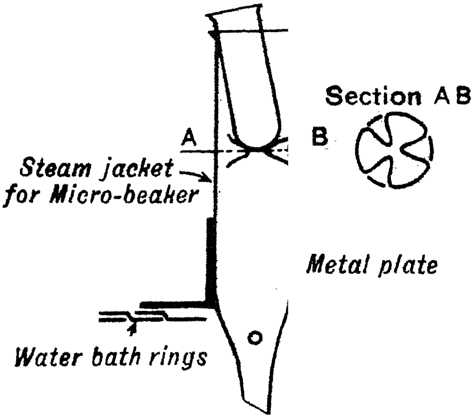


Fig. 19.

Another valuable method for concentrating solutions or evaporating to dryness directly in a centrifuge tube consists in conducting the operation on a water bath in a stream of filtered air supplied through a capillary tube fixed just above the surface of the liquid. The experimental details will be evident by reference to Fig. 20.

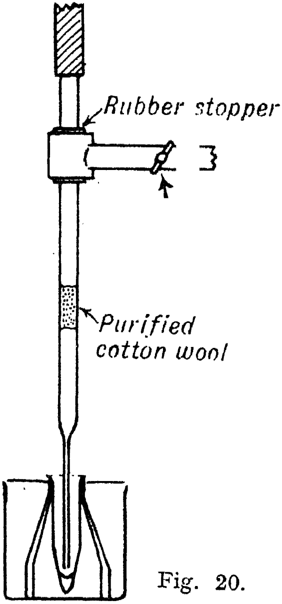


Fig. 20.

Centrifuge cones are cleaned with a feather or small test-tube brush. They are then filled with distilled water from a wash bottle, and emptied by suction using the device illustrated in Fig. 21. After suction has been started and the liquid drawn out, the tube is filled several times with distilled water without removing the suction device. Dropper pipettes are cleaned by repeatedly filling and emptying them with water, finally separating bulb and tube and rinsing both with distilled water from a wash bottle. A transfer capillary pipette is cleaned by blowing a stream of water through it from a wash bottle.

The **passage of hydrogen sulphide into a solution in a micro-centrifuge tube** is carried out by passing the gas through a fine capillary in order not to blow the solution out of the tube. The delivery tube may be prepared by drawing out part of a length of glass tubing of 6 mm. diameter to a capillary of 1 to 2 mm. bore and 10 to 20 cm. long. A plug of purified cotton

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* Suitable platinum spatulas are obtainable from Johnson, Matthey and Co. Ltd., Hatton Garden, London, E.C.1, England.

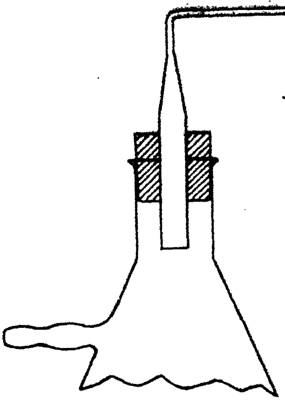

Fig. 21.

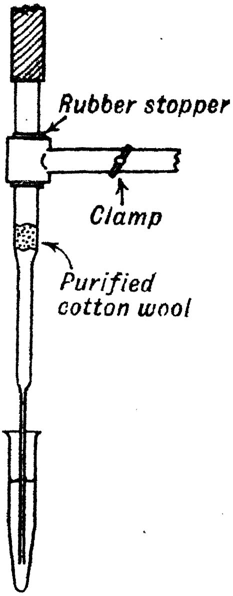

Fig. 22.

wool is inserted into the wide part of the tubing, and then the end of the capillary tube is drawn out by means of a microburner to a finer tube of 0·3 to 0·5 mm. bore and about 10 cm. long. The complete arrangement is shown in Fig. 22. Such a fine capillary delivers a stream of very small bubbles; large bubbles would throw the solution out of the micro-centrifuge tube. The flow of the hydrogen sulphide must be commenced before introducing the point of the capillary into the centrifuge cone. If this is not done, the solution will rise in the capillary and when the hydrogen sulphide is admitted, a precipitate will form in the capillary tube and clog it. The point of saturation of the solution is indicated by an increase in the size of the bubbles; this is usually after about two minutes.

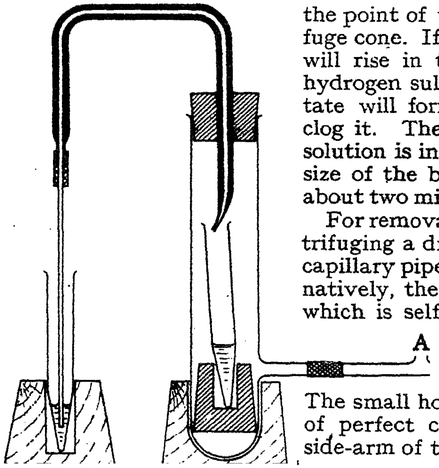

Fig. 23.

For removal of the precipitate after centrifuging a dropper pipette * or a transfer capillary pipette may be employed. Alternatively, the apparatus shown in Fig. 23, which is self-explanatory, may be used. The small hole *A* in the side tube permits of perfect control of the vacuum; the side-arm of the small test-tube is situated near the bottom so as to reduce spattering of the liquid in the tube inside the test-tube when the vacuum is released. Only *gentle* suction is applied and the opening at *A* closed with the finger; upon removing the finger, the action of the capillary siphon ceases immediately.

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* Sometimes also called a medicine dropper. The abbreviated term dropper will be used throughout this book.

The **identification of gases** obtained in the reactions for anions may be carried out in an Erlenmeyer (or conical) flask of 5 to 25 c.c. capacity provided with a stopper which carries at its lower end a " wedge point " pin constructed preferably of nickel or monel metal (Fig. 24); a small strip of impregnated test paper is placed on the loop of the pin. The stoppered flask containing the reaction mixture and test paper is placed on a water bath for about 5 minutes. An improved apparatus consists of a small flask provided with a ground-glass stopper and from the lower end of which a glass hook is fused on which the test paper can be suspended (compare Fig. 36). If it is desired to pass the evolved gas through a liquid reagent, the apparatus of Fig. 68 (see Chapter IX), proportionately reduced, may be used.

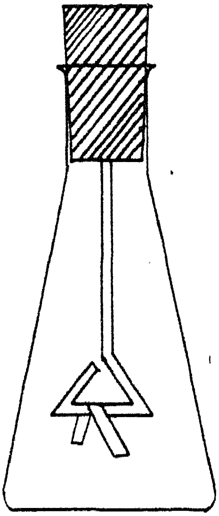

Fig. 24.

Confirmatory tests for ions may be carried out either on drop-reaction paper or upon a spot plate. The technique of spot tests is fully described in Section **II, 5.**

The following **apparatus** will be found useful :—

(i) Micro-porcelain, silica and platinum crucibles of 0·5 to 2 c.c. capacity.

(ii) Micro-nickel, monel or platinum spatula 7 to 10 cm. in length and flattened at one end.

(iii) Micro-burner.

(iv) Micro agate pestle and mortar.

(v) Magnifying lens, 5x or 10x.

(vi) A pair of forceps.

II, 5. APPARATUS REQUIRED FOR SPOT TESTS

Before dealing with the apparatus required for delicate qualitative analysis by spot tests or drop reactions, it is necessary to define clearly the various terms which are employed to express the sensitivity of a test. The **limit of identification** is the smallest amount recognisable, and is usually expressed in **micro-grams** or **gamma** (γ), one gamma being the thousandth part of a milligram or one millionth of a gram. Recently the term μg. (micro-gram) has been proposed to replace γ, and the new term will be employed throughout this book.

$$1\ \mu\text{g.} = 1\gamma = 0{\cdot}001\ \text{mg.} = 10^{-6}\ \text{g.}$$

Throughout the text the term **sensitivity** will be employed synonymously with limit of identification. The **concentration limit** is the greatest dilution in which the test gives positive results ; it is expressed as a ratio of substance to solvent. For these two terms to be comparable, a standard size drop must be used in carrying out the test. Throughout this book, unless otherwise stated, sensitivity will be expressed in terms of the standard drop of 0·05 c.c.

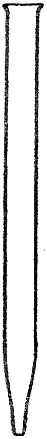

Fig. 25.
One third actual size.

The **removal and addition of drops** of test and reagent solutions is most simply carried out by using glass tubing, about 20 cm. long and 3 mm. diameter; drops from these tubes have an approximate volume of 0·05 c.c. The dropper pipette and transfer capillary pipette described in Section **II, 4** may also be used. A useful glass pipette, about 20 cm. long, may be made from 4 mm. tubing and drawn out at one end in the flame; the drawn-out ends of these pipettes may be made of varying bores (see Fig. 25). A liberal supply of glass tubes and pipettes should always be kept with the constricted end downwards, preferably in a beaker about 10 cm. high.

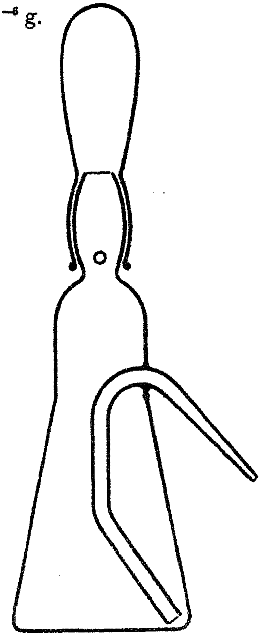

Fig. 26.
One half actual size.

Very small and even-sized drops are obtained by means of **platinum wire loops** ; the size of the loop can be varied, and by calibrating the sizes (by weighing the drops delivered) the amount of liquid delivered is fairly accurately known. The various loops are made by bending over and soldering the platinum wires of appropriate thickness : the wires should be attached in the usual manner to a length of glass rod or tubing and kept in Pyrex or Monax test-tubes fitted with corks or rubber stoppers and labelled with the particulars of the size of drop delivered. It must be pointed out that new smooth platinum wire allows liquids to drop off too readily and hence it is essential to roughen it by dipping it repeatedly into platinic chloride solution and heating to glowing in the flame.

Reagent solutions can be added from **dropping bottles** of about 50 c.c. capacity. A stock bottle for water and for solutions, which do not deteriorate on keeping, that permits the facile addition in drops is shown in Fig. 26. It consists of a Pyrex flask into which a tube with a capillary end has been fused and a drawn-out neck over which a small rubber bulb is placed ; there is a small hole in the neck to admit air.

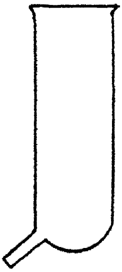

Fig. 27.
Actual size.

Digestion with acid or solvent of solid samples may be carried out in small crucibles heated on a metal hot plate (compare Section **II, 4**) or in the glass apparatus shown in Fig. 27. The latter is heated over a micro-burner, and then rotated so that the superhatant liquid or solution may be poured off drop-wise without danger or loss.

Spot tests may be carried out in a number of ways : on a spot plate, in a micro-crucible or micro-test-tube, or on filter paper. Gas reactions are carried out in special apparatus.

Spot plates are made from glazed porcelain and usually contain 6 to 12 adjacent depressions of equal size that hold 0·5 to 1 c.c. of liquid. It is advisable, however, to have several drop plates with depressions of different sizes. The white porcelain background enables very small colour changes to be seen in reactions that give coloured products; the colour changes are more readily perceived by carrying out blank tests in adjacent cavities of the spot plates. Where light-coloured or colourless precipitates or turbidities are formed, it is better to employ black spot plates, or shallow black porcelain dishes or small watch glasses on black shiny paper. Recently transparent spot plates of resistance glass have become available; these may be placed upon shiny paper of suitable colour. Traces of turbidity and of colour are also readily distinguished in micro-test-tubes about 3 cm. long and 3·5 mm. diameter ; a suitable stirrer is shown in Fig. 17. As a general rule, micro-test-tubes are used for testing diluted solutions so as to obtain a sufficient

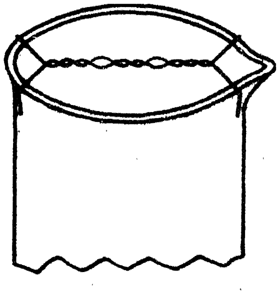

Fig. 28.

depth of colour. Alternatively, micro-centrifuge tubes may be used.

A method for warming the liquid in a micro-centrifuge tube has already been described (Section **II, 4**). When the liquid is contained in a micro-test tube the apparatus shown in Fig. 28 is employed. This is constructed of thin aluminium or nickel wire: the tubes will slip through the opening and rest on their collars. The wire holder is arranged to fit over a small beaker, which can be filled with water at a suitable temperature, and it holds two tubes to enable a parallel test to be carried out.

Where heating is essential in carrying out spot tests, micro-porcelain crucibles may be used. These may be heated inside a nickel crucible (see Fig. 18) or on an asbestos mat. Small silica watch glasses are also useful for evaporations.

It must be emphasised that all glass apparatus, including spot plates and crucibles, must be kept scrupulously clean. Cleaning is best effected by immersion in chromic-concentrated sulphuric acid mixture or in a mixture of concentrated sulphuric acid and hydrogen peroxide, followed by washing with a liberal quantity of distilled water, and drying.

The great merit of the glass and porcelain apparatus described in the previous paragraphs is that they can be employed with any strength of acid and alkali. Filter paper, however, cannot be used with strong acid solutions for the latter cause it to tear, whilst strong alkaline solutions produce a swelling of the paper. Nevertheless, for many purposes, particularly in the application of capillary phenomena, reactions carried out upon filter paper have a great advantage over glass or porcelain.

The **best filter paper to employ for most spot tests** is either Whatman drop reaction paper No. 120, double thickness or Whatman No. 3. MM., 1st quality. Both of these papers have the desirable property of rapidly absorbing the drops without too much spreading as is the case with thinner papers. These papers cannot be used for a few spot reactions because of the traces of impurities (*e.g.*, iron and phosphate) that they contain; in such cases quantitative filter paper (Whatman No. 42 or, better, the hardened variety No. 542) must be employed. The papers may be employed in rectangles (5 × 2·5 cm.) or in squares (2 × 2 cm.) or, for the quantitative filter papers, in the original circular shape; they are best stored in Petri dishes.

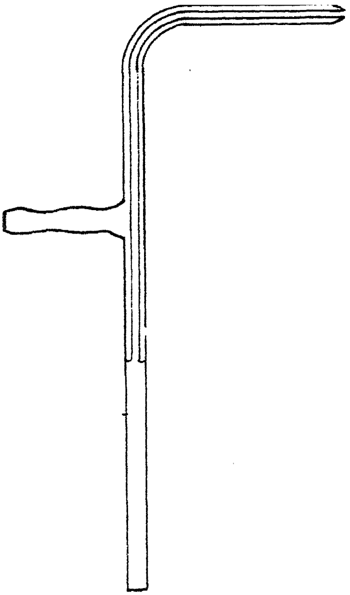

Fig. 29.
One half actual size.

Impregnated reagent papers can be made by immersing strips of quantitative filter paper in the reagent solution of suitable concentration, and drying in an electric or steam oven. Another method is to spray the reagent on the paper; the simple spray shown in Fig. 29 is suitable for this purpose. In some cases impregnants are not very stable in paper; thus soluble alkali salts frequently decompose rather easily in paper. The difficulty can sometimes be surmounted by the use of less soluble salts of other metals (B. L. Clarke and H. W. Hermance, 1937). In this way the concentration of the reactive ion can be regulated automatically by the proper selection of the impregnating salt, and the specificity of the test can be greatly improved by thus restricting the number of possible reactions. For example, potassium xanthate (see under Molybdenum, Section **VII, 4,** reaction *8*) has little value as an impregnating agent in test-papers since it decomposes rapidly and is useless after a few days. When, however, cadmium xanthate is used a paper is obtained which gives sensitive reactions only with copper and molybdenum and will keep for months. Similarly the colourless cadmium and zinc ferrocyanides offer parallel advantages as sources of ferrocyanide ions. An excellent example is paper impregnated with zinc, cadmium or antimony sulphides: such papers are stable, each with its maximum sulphide ion concentration (controlled by its solubility product) and hence precipitates only those metallic sulphides whose solubility products are sufficiently low. Antimonious sulphide paper precipitates only silver, copper and mercury in the presence of lead, cadmium, tin, iron, nickel, cobalt and zinc. Such papers are ordinarily prepared by direct precipitation of the reagent substance on the paper fibres; the paper is first soaked in a solution containing one of the ions to be precipitated, then immersed quickly in a solution containing the other ion, washed thoroughly and dried. For example, cadmium sulphide paper is prepared by using a 10 per cent solution of cadmium acetate, followed by precipitation with 5 per cent sodium sulphide solution; the final washing is done with dilute acetic acid to remove any traces of sodium sulphide. It might be supposed that the use of " insoluble " reagents would slow up the reaction rate. This retardation is not significant when paper is the medium because of the state of fine division and the great surface available. Reduction in sensitivity becomes appreciable only when the solubility products of the reagent and the reaction product approach the same order. This is naturally avoided in the selection of the reagent.

The reactions are carried out by adding drops of the test solution from the capillary pipettes, etc., to the reagent paper. The resulting change of colour may occur at once, or may develop after the application of a further reagent such as, for example, ammonia. It is best not to allow the test solution to drop on to the paper, but to allow it to run slowly from a capillary tip (0·2–1 mm. diameter) by touching the tip on the paper. The test drop then enters over a minute area, precipitation or adsorption of the reaction product taking place in the immediate surrounding region, where it remains fixed in the fibres whilst the clear liquid spreads radially outwards by capillarity. A concentration of the coloured product, which would otherwise be spread over the whole area originally wetted by the test drop, is obtained, rendering minute quantities distinctly visible. Thus a very much greater sensitivity is obtained than by adding a free drop of the solution.

The problem of **separating solid and liquid phases** either before or after taking a sample drop of the test solution frequently arises in spot analysis. Where there is a comparatively large volume of liquid and the solid matter is required, centrifuging in a micro-centrifuge tube (Section

II, 4) may be employed. Alternatively, centrifuging may be carried out in a sintered glass filter tube (Fig. 30) placed in a suitable size test-tube; this device simplifies the washing of a precipitate. If the solid is not required, the liquid may be taken up in a glass pipette by sucking through a small pad of purified cotton wool placed in the constricted capillary end; upon removing the cotton wool and wiping the pipette, the liquid may be delivered clear and free from suspended matter.

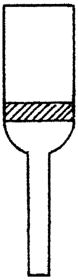

Fig. 30.
Actual size.

A useful **filter pipette** is shown in Fig. 31. It is constructed of tubing of 6 mm. diameter. A rubber bulb is attached to the short arm *A*; the arm *B* is ground flat, whilst the arm *C* is drawn out to a fine capillary; a short piece of rubber tubing is fitted over the top of *B*. For filtering, a disc of filter paper of the same diameter as the outside diameter of the tube (cut out from filter paper by means of a sharp cork borer or by a hand punch) is placed on the flat ground surface of *B*, the tube *F* placed upon it and then held in position by sliding the rubber tubing just far enough over the paper to hold it when the tube *F* is removed. The filter pipette may be used either by placing a drop of the solution on the filter disc or by immersing the tube end *B* into the crucible, test-tube or receptacle containing the solution to be filtered. The bulb is squeezed by the thumb and middle finger, and the dropper point closed with the fore-finger thus allowing the solution to be drawn through the paper when the bulb is released. To release the drops of filtered liquid thus obtained, the instrument is inverted over the spot plate, etc., in an inclined position with the bulb uppermost. Manipulation of the bulb again forces the liquid in the tip on to the spot plate, etc. The precipitate on the paper can be withdrawn for any further treatment by simply sliding the rubber tubing *D* down over the arm *B*.

Another method involves the use of an **Emich filter stick** fitted through a rubber stopper into a thick-walled suction tube, which contains a micro-test tube to collect the filtrate (Fig. 32). The filter stick contains a small pad of asbestos.

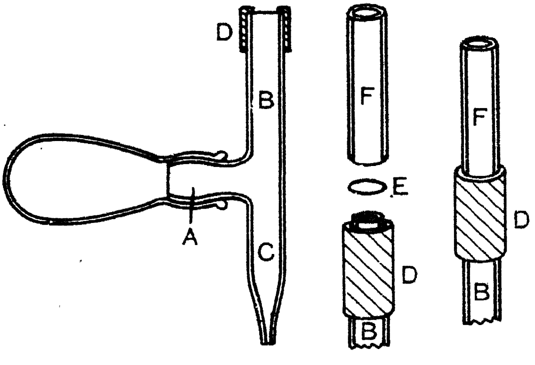

Fig. 31.

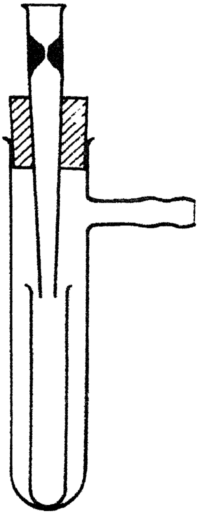

Fig. 32. Two thirds actual size.

Where the filter paper (or watch glass) must be **heated in steam,** the apparatus shown in Fig. 33 may be employed. The filter paper (or watch glass) is placed on the side-arm support. The apparatus may also be employed for the volatilisation of low boiling point liquids. **Fusion** and solution of a melt may be carried out either in a platinum wire loop or in a platinum spoon (0·5–1 c.c. capacity) attached to a heavy platinum wire and fused into a glass holder.

Gas reactions are carried out in specially devised apparatus. Thus in testing for carbonates, sulphides, etc., it is required to absorb the gas liberated in a drop of water or reagent solution. The apparatus is shown in Fig. 34, and consists of a micro-test tube of about 1 c.c. capacity, which can be closed with a small ground glass stopper fused to a glass knob. The reagent and test solution or test solid are placed in the bottom of the tube, and a drop of the reagent for the gas is suspended on the knob of the stopper. The gas is evolved in the tube, if necessary, by gentle warming, and is absorbed by the reagent on the knob. Since the apparatus is closed, no gas can escape, and if sufficient time is allowed it is absorbed quantitatively by the reagent. A drop of water may replace the reagent on the stopper; the gas is dissolved, the drop may be washed on to a spot plate or into a micro-crucible and treated with the reagent. The apparatus, shown in Fig. 35, which is closed by a rubber stopper is sometimes preferable, particularly when minute quantities of gas are concerned; the glass tube, blown into a small bulb at the lower end, may be raised or lowered at will, whilst the change of colour and reaction products may be rendered more easily visible by filling the bulb with gypsum or magnesia powder. In some reactions, *e.g.*, in testing for ammonia, it may be desirable to suspend a small strip of reagent paper from a glass hook fused to the stopper as in Fig. 36. When a particular gas has to be identified in the presence of other gases, the apparatus shown in Fig. 37 should be used; here the stopper for the micro-test tube consists of a small glass funnel on top of which the impregnated filter paper is laid in order to absorb the gas. The impregnated filter paper permits the passage of the indifferent gases and only retains the gas to be tested by the formation of a non-volatile compound that can be identified by means of a spot test. Another useful apparatus is shown in Fig. 38; it consists of a micro-test tube into which is placed a loosely-fitting glass tube narrowed at both ends. The lower capillary end is filled to a height of about 1 mm. with a suitable reagent solution; if the gas liberated

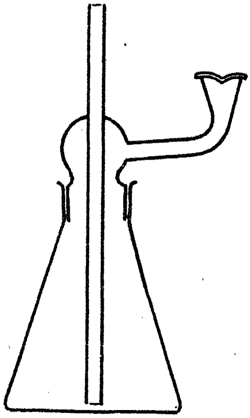

Fig. 33. One quarter actual size.

forms a coloured compound with the reagent, it can easily be seen in the capillary.

Where **high temperatures or glowing** are necessary for the evolution of the gas, a simple hard glass tube supported in a circular hole in an asbestos or " uralite " plate (Fig. 39) may be used. The open end of the tube should be covered by a small piece of reagent paper and kept in position by means of a glass cap.

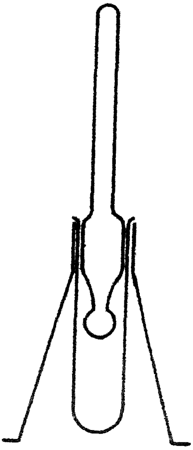

Fig. 34.
Actual size.

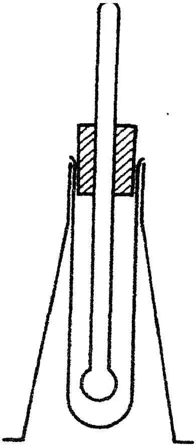

Fig. 35.
Actual size.

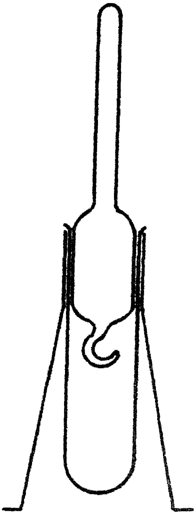

Fig. 36.
Actual size.

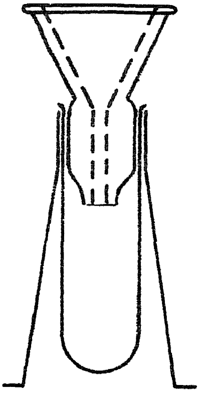

Fig. 37.
Actual size.

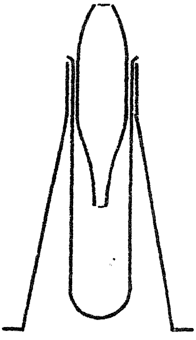

Fig. 38.
Actual size.

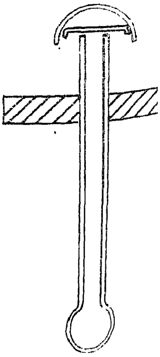

Fig. 39.
Actual size.

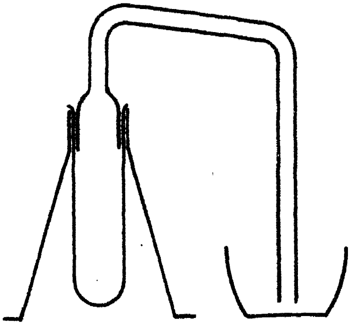

Fig. 40.
Actual size.

Micro-distillation is sometimes required, *e.g.*, in the chromyl chloride test for a chloride (see Section **IV, 14**, reaction *5*). The apparatus depicted in Fig. 40 may be employed for distilling very small quantities of substance. A micro-crucible or micro-centrifuge tube may be used as a receiver.

In Chapters III, IV and VII the experimental details for a number of elements or radicals are given. These tests are set out in 9 point type as distinct from the other reactions which are in 11 point, or, for the rarer elements, in 10 point type; they can thus be readily distinguished and this is further facilitated by the use of a dagger (†) preceding the 9 point type. The sensitivities given are, as a general rule, for a solution containing only the ion in question. It must be remembered that this is the most favourable case, and that in actual practice the presence of other ions usually necessitates a modification of the procedure, which is frequently indicated, and which, more often than not, involves a loss of sensitivity. Almost without exception each test is subject to interference from the presence of other ions, and the possibility of these interferences occurring must be taken into consideration when a test is applied. Furthermore, the sensitivities when determined upon drop-reaction paper will depend upon the type of paper used. The figures given in this book have been determined, for the most part by Feigl, chiefly with Schleicher and Schüll's spot paper. Slightly different results may be given by the Whatman papers recommended in this volume because of the different diffusion rates. For purposes of reference the following equivalent papers are tabulated :—

Schleicher and Schüll Paper	*Whatman Paper*
No. 601, "spot paper".	Drop-reaction paper, No. 120, double thickness.
No. 598.	No. 3 MM., 1st quality.
No. 589.	No. 42 or No. 542.

It is important to draw attention to the difference between the terms "specific" and "selective" when used in connexion with reagents or reactions. Reactions (and reagents), which under the experimental conditions employed are indicative of one substance (or ion) only are designated as **specific,** whilst those reactions (and reagents) which are characteristic of a comparatively small number of substances are classified as **selective.** Hence we may describe reactions (or reagents) as having varying degrees of selectivity; however, a reaction (or reagent) can be only specific or not specific.

CHAPTER III

REACTIONS OF THE METAL IONS OR CATIONS

III, 1. The Analytical Classification of the Metals.—The common metallic ions may be divided, for purposes of qualitative analysis, into a number of groups which are distinguished by the fact that the metals of any group are precipitated by a particular group reagent. Thus by the addition of a slight excess of dilute hydrochloric acid to a solution containing all

Group	*Group Reagent*	*Ions*	*Formula of Precipitate*	*Distinguishing Features*
I (*Silver group*)	Dilute HCl	Ag^+, Pb^{++}, Hg_2^{++}	$AgCl$, $PbCl_2$, Hg_2Cl_2	Chlorides insoluble in dilute HCl.
II (*Copper and arsenic groups*)	H_2S in presence of dilute HCl	Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, Sn^{++}, As^{+++} Sb^{+++}, Sn^{++++}	HgS, PbS, Bi_2S_3, CuS, CdS, SnS, As_2S_3, Sb_2S_3, SnS_2	Sulphides insoluble in dilute HCl.
IIIA (*Iron group*)	NH_4OH in presence of NH_4Cl	Al^{+++}, Cr^{+++}, Fe^{+++}	$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$	Hydroxides pptd. by NH_4OH in presence of NH_4Cl.
IIIB (*Zinc group*)	$(NH_4)_2S$ in presence of NH_4OH and NH_4Cl	Ni^{++}, Co^{++}, Mn^{++}, Zn^{++}	NiS, CoS, MnS, ZnS	Sulphides ppd. by $(NH_4)_2S$ in presence of NH_4Cl.
IV (*Calcium group*)	$(NH_4)_2CO_3$ in presence of NH_4OH and NH_4Cl	Ba^{++}, Sr^{++}, Ca^{++}	$BaCO_3$, $SrCO_3$, $CaCO_3$	Carbonates pptd. by $(NH_4)_2CO_3$ in presence of NH_4Cl.
V (*Alkali group*)	No particular reagent	Mg^{++}, Na^+, K^+, (Li^+), NH_4^+	Mg^{++}, Na^+, K^+, (Li^+), NH_4^+, in solution	Ions not pptd. in previous groups.

the common metallic ions, a precipitate is obtained consisting of the chlorides of silver, lead and mercurous mercury. These metal ions are therefore classed together in Group I; their chlorides are insoluble in dilute hydrochloric acid. Similarly by the use of the appropriate group reagents, the remaining metallic ions are separated into different groups. In general, it may be stated that the classification is based upon the varying solubilities of the chlorides, sulphides, hydroxides and carbonates.

The various groups are summarised in the table on the previous page.

Ammonium is detected in the original substance by boiling a small portion with sodium hydroxide solution before carrying out the separation of the metal ions into groups.

It is assumed in the above table that the group reagents are added systematically to the solutions from which the ions of the earlier groups have been removed. Thus dilute hydrochloric acid is added to the original solution, hydrogen sulphide is passed into the filtrate from Group I, ammonium hydroxide and ammonium chloride solutions are added to the filtrate from Group II, and so on.

A knowledge of the reaction of the various ions is necessary in order to understand the processes involved in the separation of the members of the various groups and generally to appreciate the subject of qualitative analysis. A systematic account of the more common metal ions arranged in order of the groups is given in the following pages.

THE SILVER GROUP (GROUP I)

LEAD, MERCURY (OUS) AND SILVER

The compounds of these metals are characterised by their precipitation as chlorides by dilute hydrochloric acid or by a soluble chloride. Lead chloride is slightly soluble in water and hence is not completely precipitated as chloride in this group; it is therefore also found in Group II, where it is precipitated as the highly insoluble sulphide.

LEAD, Pb

Lead is a bluish-grey metal with a density of 11·48. It is readily dissolved by dilute nitric acid:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O.$$

With concentrated nitric acid, a protective film of lead nitrate, which is insoluble in this acid, prevents complete solution. Dilute hydrochloric acid and dilute sulphuric acid have little action owing to the formation of protective films of lead chloride and sulphate respectively.

III, 2. REACTIONS OF THE LEAD ION, Pb^{++}

Use a solution of lead nitrate, $Pb(NO_3)_2$, or of lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$ (abbreviated to $Pb\bar{A}_2,3H_2O$), acidified with a little acetic acid $H.C_2H_3O_2$ (or $H\bar{A}$).*

1. **Dilute Hydrochloric Acid**: white precipitate of lead chloride $PbCl_2$, formed only in cold and not too dilute solution:

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3.$$

The precipitate is soluble in hot water (33·4 g. and 9·9 g. per litre at 100° and 20° respectively), but separates out again in needles when the solution is cooled. It is also soluble in concentrated hydrochloric acid and in concentrated alkali chloride solutions owing to the formation of complex compounds (compare Section **I, 19**); these are decomposed on dilution with water with the separation of lead chloride:

$$PbCl_2 + HCl = H[PbCl_3]; \quad PbCl_2 + 2HCl \rightleftharpoons H_2[PbCl_4].$$

2. **Potassium Iodide Solution**: yellow precipitate of lead iodide PbI_2, moderately soluble in boiling water to yield a colourless solution from which it separates on cooling in golden yellow plates. It is also soluble in excess of potassium iodide solution forming a complex salt, which is decomposed on dilution with deposition of lead iodide.

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3.$$
$$PbI_2 + 2KI = K_2[PbI_4].$$

3. **Dilute Sulphuric Acid**: white precipitate of lead sulphate $PbSO_4$, insoluble in excess, but soluble in a concentrated solution of ammonium acetate (due to the formation of lead acetate, which is little ionised in the presence of excess of acetate ions (see Common Ion Effect, Section **I, 14**)) or in an ammoniacal solution of ammonium tartrate or in a warm solution of sodium thiosulphate.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$
$$PbSO_4 + 2NH_4.C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4.$$

4. **Potassium Chromate Solution**: yellow precipitate of lead chromate $PbCrO_4$, insoluble in acetic acid and in ammonia solution, but soluble in alkali hydroxides and in nitric acid. Lead chromate is quantitatively precipitated from an ammonium acetate solution of lead sulphate (reaction *3*).

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* It is recommended that the test solutions employed in the study of the reactions of the cations and anions described in Chapters III and IV be prepared as detailed in the Appendix (Section **A, 3**). These contain 10 milligrams of the cation or anion per c.c.

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3.$$

$$PbCrO_4 + 4NaOH = Na_2[PbO_2] + Na_2CrO_4 + 2H_2O.$$

5. **Hydrogen Sulphide** : black precipitate of lead sulphide PbS. The precipitate is often red in the presence of hydrochloric acid ; this is due to the initial formation of lead sulphochloride Pb_2SCl_2, which is decomposed on dilution and by passage of excess of hydrogen sulphide forming black lead sulphide.

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3.$$

$$2PbCl_2 + H_2S = Pb_2SCl_2 + 2HCl.$$

The precipitate of lead sulphide is insoluble in solutions of alkali sulphides, but soluble in hot dilute nitric acid :

$$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S.$$

It is converted into white lead sulphate $PbSO_4$ on treatment with hydrogen peroxide :

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

The great insolubility of lead sulphide in water (4·9 × 10^{-11} g. per litre) explains why hydrogen sulphide is such a sensitive reagent for the detection of lead, and why it can be detected in the filtrate from the separation of the sparingly soluble lead chloride in dilute hydrochloric acid.

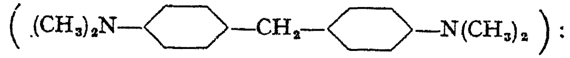
6. **Sodium Hydroxide Solution** : white precipitate of lead hydroxide $Pb(OH)_2$, soluble in excess of the reagent to form sodium plumbite :

$$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3 ;$$

$$Pb(OH)_2 + 2NaOH = Na_2[PbO_2] + 2H_2O.$$

Ammonium hydroxide solution yields the white hydroxide, insoluble in excess of the precipitant.

†*7.* **Tetramethyldiamino-diphenylmethane** (or **Arnold's Base**) **Reagent**



a blue oxidation product is formed under the conditions given below.

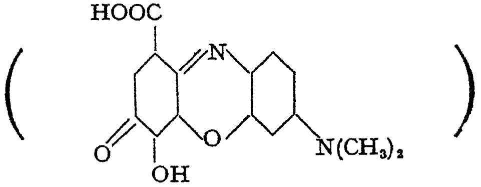
Place a drop of " 10-volume " hydrogen peroxide upon drop-reaction paper, add a drop of dilute ammonia solution and immediately a drop of the test solution. Hold the paper over a source of steam or allow it to stand in the air for several minutes: lead peroxide is thus formed and most of the excess of hydrogen peroxide is rendered harmless. Add a drop of the " tetra-base " reagent ; a blue colour develops.

Sensitivity : 1 μg Pb. Concentration limit : 1 in 50,000.

Mercury, copper, cadmium, arsenic, antimony and tin do not affect the test, but bismuth, when its concentration is more than 11 times that of the lead, interferes.

The **reagent** is prepared by dissolving 0·05 g. of the " tetra-base " in 10 c.c. of glacial acetic acid and diluting to 100 c.c. with distilled water.

†*8*. Gallocyanine Reagent



deep violet precipitate of unknown composition. The test is applicable to finely-divided lead sulphate precipitated on filter paper.

Place a drop of the test solution upon drop-reaction paper, followed by a drop each of 1 per cent aqueous pyridine and the gallocyanine reagent (blue). Remove the excess of the reagent by placing several filter papers beneath the drop-reaction paper and adding drops of the pyridine solution to the spot until the wash liquid percolating through is colourless; move the filter papers to a fresh position after each addition of pyridine. A deep violet spot is produced.

Sensitivity : 1–6 μg. Pb. Concentration limit : 1 in 50,000.

In the **presence of silver, bismuth, cadmium or copper,** proceed as follows. Transfer a drop of the test solution to a drop-reaction paper and add a drop of 2*N*-sulphuric acid to fix the lead as lead sulphate. Remove the soluble sulphates of the other metals by washing with about 3 drops of 2*N*-sulphuric acid, followed by a little rectified spirit, Dry the paper on a water bath, and then apply the test as detailed above.

The **reagent** consists of a 1 per cent aqueous solution of gallocyanine.

†*9*. **Stannous Chloride-Potassium Iodide Reagent :** deep orange-red complex, $2PbI_2,SnI_2$, formed. The test is given by lead sulphate precipitated on filter paper ; it can therefore be employed in the presence of other metals.

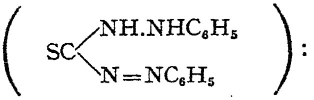
Place a drop of *N*-sulphuric acid upon a piece of thick drop-reaction paper (Whatman No. 3 MM., 1st quality) and allow it to diffuse into the paper. Introduce a drop of the test solution into the middle of the spot, followed by another drop of *N*-sulphuric acid in order to convert all the lead into the sulphate, which remains in the paper. Wash away any soluble salts with water added from a fine capillary tube. Then add a drop of the reagent to the middle of the spot where the lead sulphate was deposited. A more or less intense orange-red colouration is produced.

Sensitivity : 10 μg. Pb. Concentration limit : 1 in 5,000.

In the presence of bismuth and lead a brown spot is formed, which consists of a compound of bismuth and lead iodides produced in consequence of the adsorption of some bismuth by the lead sulphate. Lead and bismuth are thus simultaneously identified.

The **reagent** must be freshly prepared as follows. Stannous chloride solution, prepared from pure tin and concentrated hydrochloric acid, is treated with saturated potassium iodide solution until upon shaking the mixture is converted into a pale-yellow mass. A saturated solution of cadmium nitrate is then added dropwise until the pale-yellow mass dissolves. The reagent is stable in the presence of water. In the presence of sulphuric acid, yellow stannous iodide is precipitated; for this reason a drop of 10 per cent barium chloride solution is sometimes added before the washing process.

†*10.* Diphenylthiocarbazone (or Dithizone) Reagent



$$\left(SC\begin{matrix} \diagup NH.NHC_6H_5 \\ \diagdown N=NC_6H_5 \end{matrix} \right):$$

brick-red complex salt in neutral, ammoniacal, alkaline or alkali-cyanide solution.

Shake a drop of the test solution in a micro test-tube with a drop of the dithizone reagent. The green reagent assumes a red colour.

Sensitivity: 0·04 μ g. Pb (in neutral solution). Concentration limit: 1 in 1,250,000.

Since the reaction takes place in solutions containing alkali cyanide and alkali tartrate, it is applicable in the presence of many heavy metals (silver, mercury, copper, cadmium, antimony, nickel, zinc, etc.).

The **reagent** is prepared by dissolving 1–2 mg. of dithizone in 100 c.c. of carbon tetrachloride or of chloroform. It does not keep well.

Dry Tests

(i) *Blowpipe test.*—When a lead salt is heated with alkali carbonate upon charcoal, a malleable bead of lead (which is soft and will mark paper), surrounded with a yellow incrustation of lead monoxide, is obtained.

(ii) *Flame test.*—Pale blue (inconclusive).

MERCURY Hg

Mercury is a silvery-white, liquid metal at the ordinary temperature and has a density ($d_{4^\circ}^{0^\circ}$) of 13·595. It is unaffected by treatment with dilute hydrochloric or dilute sulphuric acid, but reacts readily with nitric acid. Cold dilute nitric acid and excess of mercury yield mercurous nitrate, whilst with excess of the hot concentrated acid mercuric nitrate is produced:

$$6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO + 4H_2O;$$
$$Hg + 4HNO_3 = Hg(NO_3)_2 + 2NO_2 + 2H_2O.$$

With hot concentrated sulphuric acid, mercurous or mercuric sulphate is formed according as the metal or the acid is present in excess:

$$2Hg + 2H_2SO_4 = Hg_2SO_4 + SO_2 + 2H_2O;$$
$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

Mercury forms two series of salts: the mercurous compounds, corresponding to mercurous oxide Hg_2O and containing the bivalent mercurous group Hg_2^{++} (—Hg—Hg—), and the mercuric compounds, corresponding to mercuric oxide and containing the bivalent ion Hg^{++}.

III, 3. REACTIONS OF THE MERCUROUS ION, Hg_2^{++}

Use a solution of mercurous nitrate, $Hg_2(NO_3)_2,2H_2O$.

1. **Dilute Hydrochloric Acid**: white precipitate of mercurous chloride (calomel) Hg_2Cl_2, insoluble in hot water and in cold dilute acids, but soluble in aqua regia, whereby it is converted into mercuric chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3.$$

The precipitate becomes black when ammonium hydroxide solution is poured over it, due to the production of aminomercuric chloride (" infusible white precipitate ") and finely divided mercury (black) ; this black mixture is soluble in aqua regia with the formation of mercuric chloride :

$$Hg_2Cl_2 + 2NH_4OH = Hg(NH_2)Cl + Hg + NH_4Cl + 2H_2O ;$$

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O ;$$

$$2Hg(NH_2)Cl + 3Cl_2 = 2HgCl_2 + 4HCl + N_2 ;$$

$$Hg + Cl_2 = HgCl_2.$$

2. **Potassium Iodide Solution**: yellowish-green precipitate of mercurous iodide Hg_2I_2, which yields soluble potassium mercuri-iodide $K_2[HgI_4]$ and black finely divided mercury with excess of the reagent.

$$Hg_2(NO_3)_2 + 2KI = Hg_2I_2 + 2KNO_3 ;$$

$$Hg_2I_2 + 2KI = K_2[HgI_4] + Hg.$$

3. **Potassium Chromate Solution**: brown amorphous precipitate of mercurous chromate Hg_2CrO_4 in the cold, which is converted into a red crystalline form on boiling.

$$Hg_2(NO_3)_2 + K_2CrO_4 = Hg_2CrO_4 + 2KNO_3.$$

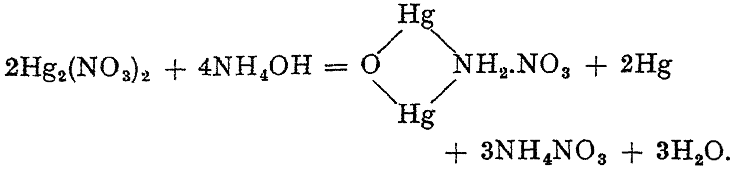
4. **Hydrogen Sulphide**: immediate black precipitate of mercuric sulphide HgS and mercury (difference from mercuric salts).

$$Hg_2(NO_3)_2 + H_2S = 2HNO_3 + HgS + Hg.$$

5. **Sodium Hydroxide Solution**: black precipitate of mercurous oxide Hg_2O, insoluble in excess of the precipitant.

$$Hg_2(NO_3)_2 + 2NaOH = Hg_2O + 2NaNO_3 + H_2O.$$

6. **Ammonium Hydroxide Solution** : black precipitate, consisting of a mercuric amino salt and finely divided mercury.



$$2Hg_2(NO_3)_2 + 4NH_4OH = \mathrm{O}\begin{smallmatrix}\diagup\mathrm{Hg}\diagdown\\ \diagdown\mathrm{Hg}\diagup\end{smallmatrix}\mathrm{NH_2.NO_3} + 2Hg + 3NH_4NO_3 + 3H_2O.$$

7. **Stannous Chloride Solution** : grey, finely-divided mercury is obtained with excess of the reagent.

$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = 2Hg + SnCl_4 + 2HNO_3.$$

8. **Potassium Nitrite Solution :** mercury separates as a dark grey (or black) precipitate (distinction from mercuric salts).

† The spot test technique is as follows. Place a drop of the faintly acid test solution upon drop-reaction paper and add a drop of concentrated potassium nitrite solution. A black (or dark grey) spot is produced. The test is specific. Coloured ions yield a brown colouration which may be washed away, leaving the black spot.

Dry Tests

See under Mercuric Ions, Section **III, 6.**

SILVER, Ag

Silver is a white, malleable and ductile metal. It is insoluble in dilute hydrochloric and sulphuric acids, but dissolves readily in nitric acid (2 : 1) and in boiling concentrated sulphuric acid :

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O\,;$$
$$Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

III, 4. REACTIONS OF THE SILVER ION, Ag^+

Use a solution of silver nitrate, $AgNO_3$.

1. **Dilute Hydrochloric Acid** : white, curdy precipitate of silver chloride AgCl, which darkens on exposure to light. The precipitate is insoluble in water (solubility, $1{\cdot}5 \times 10^{-3}$ g. per litre) and in acids (including nitric acid), but is soluble in dilute ammonium hydroxide solution owing to the formation of the complex ion, $[Ag(NH_3)_2]^+$ (see Section **I, 20**) ; it is precipitated from the ammoniacal solution by the addition of dilute nitric acid or of potassium iodide solution.

$$AgNO_3 + HCl = AgCl + HNO_3;$$
$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl;$$
$$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl + 2NH_4NO_3;$$
$$[Ag(NH_3)_2]\,Cl + KI = AgI + KCl + 2NH_3.$$

Silver chloride is also soluble in potassium cyanide solution (*highly poisonous*) and in sodium thiosulphate solution :

$$AgCl + 2KCN = K[Ag(CN)_2] + KCl.$$
$$2AgCl + 3Na_2S_2O_3 = Na_4[Ag_2(S_2O_3)_3] + 2NaCl.$$

2. **Potassium Iodide Solution** : yellow precipitate of silver iodide AgI, insoluble in ammonium hydroxide solution, but readily soluble in solutions of potassium cyanide and of sodium thiosulphate.

$$AgNO_3 + KI = AgI + KNO_3;$$
$$AgI + 2KCN = K[Ag(CN)_2] + KI.$$

3. **Potassium Chromate Solution** : red precipitate of silver chromate Ag_2CrO_4, insoluble in dilute acetic acid, but soluble in dilute nitric acid and in ammonium hydroxide solution.

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3.$$

† The spot technique is as follows. Place a drop of the test solution on a watch glass or on a spot plate, add a drop of ammonium carbonate solution and stir (this renders any mercurous mercury or lead ions unreactive by precipitation as the highly insoluble carbonates). Remove the drop of the clear liquid and place it on drop-reaction paper together with a drop of the potassium chromate reagent. A red ring of silver chromate is obtained.

Sensitivity : 2 μg. Ag. Concentration limit : 1 in 25,000.

Alternatively, the reaction with the clear solution may be carried out on a spot plate, when red silver chromate is precipitated.

The **reagent** consists of a 1 per cent solution of potassium chromate in *N*-acetic acid.

4. **Hydrogen Sulphide** : black precipitate of silver sulphide Ag_2S, insoluble in water (solubility, 1×10^{-11} g. per litre) and in ammonium hydroxide solution, but soluble in hot dilute nitric acid.

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3.$$
$$3Ag_2S + 8HNO_3 = 6AgNO_3 + 2NO + 3S + 4H_2O$$

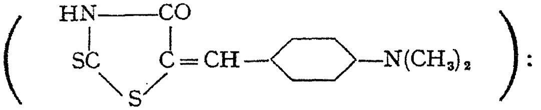
5. **Sodium Hydroxide Solution** : brown precipitate of silver oxide Ag_2O, insoluble in excess of the precipitant.

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O.$$

6. **Ammonium Hydroxide Solution** : white precipitate at first which quickly passes into brown silver oxide Ag_2O, soluble in excess of the precipitant.

$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O.$$

†7. **para-Dimethylamino-benzylidene-rhodanine Reagent**



: red-violet salt in faintly acid solution. Mercury, cuprous gold, platinum and palladium salts form similar compounds and therefore interfere.

Spot the test solution on drop reaction paper, add 1 drop of *N*-nitric acid (to decolourise the reagent) followed by a drop of the reagent. A red-violet precipitate or stain is formed according to the silver content of the test solution.

Sensitivity : 0·02 µg. Ag. (in 0·2*N*-nitric acid). Concentration limit : 1 in 2,500,000.

Alternatively, the test may be carried out (*a*) on a spot plate or (*b*) in a micro test-tube ; in the latter case the excess of the reagent is extracted with ether or amyl alcohol when violet flecks of the silver complex will be visible under the yellow solvent layer.

If **mercury and copper are present,** treat a drop of the test solution either on drop-reaction paper or on a spot plate with a drop of dilute hydrochloric acid or of ammonium chloride solution, followed by a drop of the reagent. The silver rhodanine complex is less soluble than silver chloride and is therefore precipitated ; the mercury is held in solution as undissociated mercuric chloride.

If **gold, platinum and palladium are present,** mix on a spot plate 1 drop of the test solution with a drop of 10 per cent potassium cyanide solution and a drop of the reagent. Stir and acidify with nitric acid (1 : 4). A red colour is obtained in the presence of 2·5 µg. of silver.

The **reagent** consists of a 0·03 per cent solution of *p*-dimethylaminobenzylidene-rhodanine in acetone.

Dry Tests

Blowpipe test.—When a silver salt is heated with alkali carbonate on charcoal, a white malleable bead without an incrustation of the oxide results ; this is readily soluble in nitric acid. The solution is immediately precipitated by dilute hydrochloric acid, but not by very dilute sulphuric acid (difference from lead).

DETECTION AND SEPARATION OF METALS IN THE SILVER GROUP (GROUP I)

When the student has worked through the reactions of the metals in this group, he should attempt to identify the members of the group both singly and when present in a mixture in the solutions supplied to him by the teacher*. With the aid of the following simplified table which is directly based upon the reactions already studied, this should prove a comparatively simple task. A more detailed table will be given when all the metals have been studied.

It is important that the student should acquire the habit of recording his results in tabular form.

III, 5. Table XVII.—Analysis of the Silver Group (Group I)

<table>
<tr><td colspan="3">To the given solution (or to the solution of the substance in water), add dilute HCl in excess and filter. Discard the filtrate. Wash the precipitate, which may contain $PbCl_2$, AgCl and Hg_2Cl_2, with a little water. Boil the precipitate with much water and filter hot.</td></tr>
<tr><td colspan="2">Residue. May contain Hg_2Cl_2 and AgCl. Wash the ppt. thoroughly with hot water until the extract gives no ppt. with K_2CrO_4 solution, thus ensuring the complete removal of lead; reject the washings.
Pour warm ammonium hydroxide solution over the ppt. on the filter.</td><td rowspan="2">Filtrate. May contain $PbCl_2$ Divide into two parts:
(i) Add K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$.
(ii) Cool under tap. White crystalline ppt. of $PbCl_2$.
Lead present.</td></tr>
<tr><td>Residue. Black. $Hg + Hg(NH_2)Cl$
Mercury present.</td><td>Filtrate. May contain $[Ag(NH_3)_2]Cl$.
Acidify with dilute HNO_3. White ppt. of AgCl.
Silver present.</td></tr>
</table>

THE COPPER AND ARSENIC GROUP (GROUP II)

MERCURY (IC), LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY AND TIN

The compounds of these elements are characterised by their precipitation as sulphides by hydrogen sulphide from acid solution. The sulphides of arsenic, antimony and tin are soluble in both ammonium sulphide and in sodium hydroxide solution, whilst those of the remaining metals are practically insoluble. It is therefore usual to sub-divide this group into the copper group or Group IIA, comprising mercury, lead, bismuth, copper and cadmium, and the arsenic group or Group IIB, comprising arsenic, antimony and tin.

THE COPPER GROUP (GROUP IIA)

MERCURY, Hg

Mercury forms two series of compounds, the mercurous and mercuric, derived respectively from the oxides Hg_2O and HgO. The reactions for the former have already been described (Section **III, 3**); those for the latter are detailed below.

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* Alternatively, the mixture may be prepared by the student from the solid nitrates.

III, 6. REACTIONS OF THE MERCURIC ION, Hg^{++}

Use a solution of mercuric chloride, $HgCl_2$.

1. **Hydrogen sulphide**: initially a white, then yellow, brown and finally a black precipitate of mercuric sulphide HgS. In all cases, excess of hydrogen sulphide gives the black mercuric sulphide. The white precipitate is the chlorosulphide $Hg_3S_2Cl_2$ (or $HgCl_2,2HgS$), which is decomposed by hydrogen sulphide.

$$3HgCl_2 + 2H_2S = Hg_3S_2Cl_2 + 4HCl;$$
$$Hg_3S_2Cl_2 + H_2S = 2HCl + 3HgS;$$

The net result is: $HgCl_2 + H_2S = HgS + 2HCl$.

Mercuric sulphide is insoluble in water ($4{\cdot}6 \times 10^{-25}$ g. per litre), hot dilute nitric acid, and in solutions of alkali hydroxides and of ammonium sulphide. It is converted by hot concentrated nitric acid into the basic nitrate $2HgS,Hg(NO_3)_2$, and is readily soluble in aqua regia or in a mixture of concentrated hydrochloric acid and a little potassium chlorate.

$$3HgS + 2HNO_3 + 6HCl = 3HgCl_2 + 2NO + 3S + 4H_2O.$$

2. **Stannous Chloride Solution**: a white precipitate of mercurous chloride Hg_2Cl_2 is first obtained, which is reduced by excess of the reagent to grey-black metallic mercury.

$$2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2;$$
$$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg.$$

3. **Sodium Hydroxide Solution**: initial reddish-brown precipitate of basic chloride, converted by excess of alkali into yellow mercuric oxide.

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

4. **Ammonium Hydroxide Solution**: white precipitate of amino mercuric chloride $(NH_2)HgCl$, known as "infusible white precipitate" for it volatilises without melting.

$$HgCl_2 + 2NH_4OH = Hg(NH_2)Cl + NH_4Cl + 2H_2O.$$

5. **Potassium Iodide Solution**: red (initially yellow) precipitate of mercuric iodide HgI_2, soluble in excess of the precipitant owing to the formation of the complex salt, potassium mercuri-iodide $K_2[HgI_4]$ (compare Sections **I, 19** and **I, 20**).

$$HgCl_2 + 2KI = HgI_2 + 2KCl;$$
$$HgI_2 + 2KI = K_2[HgI_4].$$

6. **Copper.** When a piece of bright copper foil, cleansed—if necessary—by rubbing it with emery paper or by dipping it into concentrated nitric acid, is immersed into the mercuric chloride solution, it becomes coated with a grey film of mercury, which acquires a silvery appearance on rubbing (see Electrode Potentials, Section **I, 29**).

$$HgCl_2 + Cu = Hg + CuCl_2.$$

7. **Ethylenediamine Reagent:** a dark blue-violet precipitate of the complex $[Cu\,en_2]\,[HgI_4]$ is formed when a mercuric salt in neutral or faintly ammoniacal solution is treated with excess of 2 per cent potassium iodide solution, followed by the ethylenediamine reagent.

$$HgCl_2 + 4KI = K_2[HgI_4] + 2KCl;$$
$$K_2[HgI_4] + [Cu\,en_2]SO_4 = [Cu\,en_2]\,[HgI_4] + K_2SO_4$$
$$(NH_2.CH_2.CH_2.NH_2 = en).$$

The reaction is a sensitive one, but cadmium ions, which form a similar complex $[Cu\,en_2]\,[CdI_4]$, interfere.

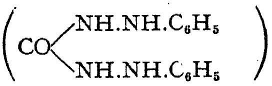
The **reagent** is prepared by treating a solution of cupric sulphate with an aqueous solution of ethylenediamine (5–6 times the theoretical quantity) until the dark blue-violet colouration, due to the $[Cu\,en_2]^{++}$ ion, appears and does not increase in intensity upon further addition of the base. The presence of excess of the latter in the reagent has no harmful influence.

†*8.* **Stannous Chloride-Aniline Test.**—Mercuric salts are reduced to grey or black metallic mercury. Large amounts of silver interfere, but bismuth and copper salts are without effect.

Treat a drop of the test solution upon drop-reaction paper or upon a spot plate with 1 drop of freshly prepared stannous chloride solution and a drop of aniline. A black to brown colouration is obtained.

Sensitivity: 1 μg. Hg. Concentration limit: 1 in 50,000.

†*9.* **Diphenyl-carbazide Reagent**



$$\left(\mathrm{CO}\begin{array}{l}\diagup\,\mathrm{NH.NH.C_6H_5}\\ \diagdown\,\mathrm{NH.NH.C_6H_5}\end{array}\right):$$

blue precipitate of undetermined composition in acid solution. The sensitivity of the test depends upon the *p*H of the solution, decreasing with decreasing *p*H. The test is specific in 0·2*N*-nitric acid solution in the absence of chromates and molybdates. In neutral or acetic acid solution, numerous elements give coloured compounds.

Place a drop of the test solution and 1 drop of 0·5*N*-nitric acid upon drop-reaction paper which has been moistened with the reagent. A violet or blue colouration appears. The reaction may also be carried out on a spot plate or in a micro test-tube.

Sensitivity: 0·2 μg. and 1·0 μg. in 0·1*N*– and 0·2*N*– nitric acid respectively. Concentration limit: 1 in 250,000 and 1 in 50,000 respectively.

The **reagent** consists of a 1 per cent solution of diphenylcarbazide in 90–100 per cent alcohol.

†*10.* **Cobalt Acetate-Ammonium Thiocyanate Reagent.**—When a solution of a mercuric salt is treated with a concentrated solution of cobalt acetate and a little solid ammonium thiocyanate, a deep-blue crystalline precipitate of cobaltous mercuri-thiocyanate $Co[Hg(CNS)_4]$ is formed. Crystallisation is sometimes slow, but may be accelerated by scratching the interior of the vessel with a glass rod.

Place a drop of the test solution on a spot plate, add a small crystal of ammonium thiocyanate followed by a little solid cobalt acetate. A blue colour is produced.

Concentration limit: 1 in 100,000.

Dry Test

All compounds of mercury when heated with a large excess (7–8 times the bulk) of anhydrous sodium carbonate in a small dry test-tube yield a grey mirror, consisting of fine drops of mercury, in the upper part of the tube. The globules coalesce when they are rubbed with a glass rod.

Note. Mercury vapour is extremely poisonous, and not more than 0·5 g. of the substance should be used in the test.

BISMUTH, Bi

Bismuth is a brittle, crystalline and reddish-white metal. It is insoluble in hydrochloric acid, but dissolves in hot concentrated sulphuric acid and in aqua regia. The best solvent is nitric acid.

$$2Bi + 6H_2SO_4 = Bi_2(SO_4)_3 + 6H_2O + 3SO_2.$$
$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 4H_2O + 2NO.$$

The salts of bismuth are derived from the sesquioxide Bi_2O_3. The hydroxide $Bi(OH)_3$ is a weak base; the salts are accordingly hydrolysed by much water (see Hydrolysis of Salts, Section **40**) yielding insoluble basic (usually bismuthyl, *i.e.*, containing the radical BiO—) salts.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

III, 7. REACTIONS OF THE BISMUTH ION, Bi^{+++}

Use a solution of bismuth nitrate, $Bi(NO_3)_3,5H_2O$, to which just sufficient nitric acid has been added to produce a clear solution.

1. **Hydrogen Sulphide**: brown precipitate of bismuth sulphide Bi_2S_3, insoluble in cold dilute acids and in ammonium sulphide solution, but soluble in hot dilute nitric acid and in boiling concentrated hydrochloric acid.

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

2. **Sodium Hydroxide Solution**: white precipitate of bismuth hydroxide $Bi(OH)_3$ in the cold with excess of the reagent, soluble in acids. It becomes yellow on boiling, due to partial dehydration.

$$Bi(NO_3)_3 + 3NaOH = Bi(OH)_3 + 3NaNO_3.$$

$$Bi(OH)_3 = BiO.OH + H_2O.$$

If hydrogen peroxide be added to the solution containing the white or yellowish-white precipitate in suspension, brown bismuthic acid $HBiO_3$ is formed:

$$BiO.OH + H_2O_2 = HBiO_3 + H_2O.$$

3. **Ammonium Hydroxide Solution**: a white basic salt, of variable composition, is precipitated. The precipitate is insoluble in excess of the reagent (distinction from copper and cadmium).

4. **Potassium Iodide Solution**: dark brown precipitate of bismuth tri-iodide, readily soluble in excess of the reagent to give a yellow solution of the complex salt $K[BiI_4]$. The complex is decomposed upon dilution giving first a precipitate of the tri-iodide and then an orange-coloured precipitate of the basic iodide (BiO)I.

$$Bi(NO_3)_3 + 3KI = BiI_3 + 3KNO_3;$$

$$BiI_3 + KI = K[BiI_4];$$

$$BiI_3 + H_2O \rightleftharpoons 2HI + (BiO)I.$$

5. **Sodium Stannite Solution**: black precipitate of finely divided bismuth in the cold. The *reagent* is prepared by adding sodium hydroxide solution to a solution of stannous chloride until the initial white precipitate of stannous hydroxide just dissolves.

$$Sn(OH)_2 + 2NaOH = Na_2[SnO_2] + 2H_2O;$$

$$2Bi(NO_3)_3 + 6NaOH + 3Na_2[SnO_2] = 2Bi + 3Na_2[SnO_3] + 6NaNO_3 + 3H_2O.$$

6. **Water.** When a solution of a bismuth salt is poured into a large volume of water, a white precipitate of the corresponding basic salt is produced, which is soluble in dilute mineral acids, but is insoluble in a solution of tartaric acid (distinction from antimony) and in solutions of alkali hydroxides (distinction from tin).

$$Bi(NO_3)_3 + H_2O \rightleftharpoons (BiO)NO_3 + 2HNO_3\,;$$

$$2Bi(NO_3)_3 + 3H_2O \rightleftharpoons (BiO)_2(OH)NO_3 + 5HNO_3 \text{ (very large excess of water)}\,;$$

$$BiCl_3 + H_2O \rightleftharpoons (BiO)Cl + 2HCl.$$

7. **Pyrogallol Reagent** ($C_6H_3(OH)_3$ — 1 : 2 : 3).—Addition of a slight excess of a concentrated solution of the reagent to a hot solution of a bismuth salt faintly acid with dilute hydrochloric acid or nitric acid, yields a yellow precipitate of the complex $Bi(C_6H_3O_3)$. It is best to add ammonia solution until the solution is alkaline to litmus paper and then dilute nitric acid until just acid. The test is a very sensitive one. Antimony interferes and should be absent.

The *reagent* is prepared as required : a suitable concentration is 0·5 gram of pyrogallol in 5 c.c. of water.

8. **Sodium Phosphate or Sodium Arsenate Solution :** white crystalline precipitate of $BiPO_4$ or $BiAsO_4$, sparingly soluble in dilute mineral acids (distinction from mercuric, lead, copper and cadmium salts).

†*9*. **Cinchonine-Potassium Iodide Reagent :** orange-red colouration or precipitate, due to bismuth-cinchonine iodide (BiI_3, cinchonine, HI), in faintly acid solution.

Moisten a piece of drop-reaction paper with the reagent and place a drop of the slightly acid test solution upon it. An orange-red spot is obtained.

Sensitivity : 0·15 μg. Bi. Concentration limit: 1 in **350,000.**

The test may also be carried out on a spot plate.

Lead, copper and mercury salts interfere because they react with the iodide. Nevertheless, bismuth may be detected in the presence of salts of these metals as they diffuse at different rates through the capillaries of the paper, and are fixed in distinct zones. When a drop of the test solution containing bismuth, lead, copper and mercury ions is placed upon absorbent paper impregnated with the reagent, four zones can be observed : (i) a white central ring, containing the mercury ; (ii) an orange ring, due to bismuth ; (iii) a yellow ring of lead iodide ; and (iv) a brown ring of iodine liberated by the reaction with copper. The thicknesses of the rings will depend upon the relative concentrations of the various metals.

Sensitivity : 10–15 μg. Bi.

The **reagent** is prepared by dissolving 1 g. of cinchonine in 100 c.c. of hot water containing a little nitric acid ; after cooling, 2 g. of potassium iodide are added.

†*10*. **Thiourea Reagent** ($NH_2.CS.NH_2$) : intense yellow colouration in the presence of dilute nitric acid. The test may be carried out on drop-

reaction paper, on a spot plate, or in a micro test-tube.

Sensitivity : 6 μg. Bi. Concentration limit : 1 in 30,000.

Mercurous mercury, silver, antimony, ferric iron and chromates interfere and should therefore be absent.

The **reagent** consists of a 10 per cent aqueous solution of thiourea.

Dry Test

Blowpipe test.—When a bismuth compound is heated on charcoal with sodium carbonate in the blowpipe flame, a brittle bead of the metal, surrounded by a yellow incrustation of the oxide, is obtained.

COPPER, Cu

Copper is a light-red metal, which is soft, malleable and ductile. It is unaffected by hydrochloric acid and by dilute sulphuric acid, but is readily attacked by dilute nitric acid and by warm concentrated sulphuric acid :

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO ;$$

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Some cuprous sulphide Cu_2S is also formed probably in accordance with the equation :

$$6Cu + 6H_2SO_4 = 4CuSO_4 + Cu_2S + SO_2 + 6H_2O.$$

There are two series of copper compounds : those derived from cuprous oxide Cu_2O (red), known as cuprous compounds and containing the ion Cu_2^{++} (or Cu^+), and those derived from cupric oxide CuO (black), known as the cupric compounds and giving rise to the ion Cu^{++}. The cuprous compounds, *e.g.*, Cu_2Cl_2, are colourless, insoluble in water and comparatively unstable, being readily oxidised to the cupric compounds ; they dissolve readily in concentrated solutions of halogen acids, forming colourless solutions which contain complex acids, such as $H_2[Cu_2Cl_6]$. Cupric salts, when dissolved in water, yield blue or green solutions ; the anhydrous salts are white or yellow.

III, 8. REACTIONS OF THE CUPRIC ION, Cu^{++}

Use a solution of cupric sulphate, $CuSO_4,5H_2O$.

1. **Hydrogen Sulphide** : a black precipitate of cupric sulphide CuS is obtained in neutral or preferably acid (HCl) solutions. The precipitate is soluble in hot dilute nitric acid and in potassium cyanide solution ; in the latter case a complex salt, potassium cupro-cyanide $K_3[Cu(CN)_4]$ is formed. Cupric sulphide is insoluble in boiling dilute sulphuric acid (distinction from cadmium).

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

$$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO + 3S.$$

Cupric sulphide tends to form a colloidal solution and pass through filter paper. This is avoided by carrying out the precipitation in the presence of hydrochloric acid or some other electrolyte. It also tends to oxidise to the soluble sulphate when exposed to the air in the moist state : this is prevented by washing the precipitate with acidulated hydrogen sulphide water.

2. **Sodium Hydroxide Solution** : blue precipitate of cupric hydroxide $Cu(OH)_2$, insoluble in moderate excess of the reagent, and converted on boiling into black cupric oxide.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$
$$Cu(OH)_2 = CuO + H_2O.$$

In the presence of a solution of tartaric acid or of citric acid, cupric hydroxide is not precipitated by solutions of caustic alkalis, but the solution is coloured an intense blue. If the alkaline solution is treated with certain reducing agents, such as hydroxylamine, hydrazine, glucose and acetaldehyde, yellow cuprous hydroxide is precipitated from the warm solution, which is converted into red cuprous oxide Cu_2O on boiling. The alkaline solution of cupric salt containing tartaric acid is usually known as *Fehling's solution* ; it contains the complex salt $Na_4[(C_4H_2O_6Na)_2Cu]$.

3. **Ammonium Hydroxide Solution** : pale blue precipitate of basic salt, soluble in excess of the precipitant with the formation of a deep blue solution containing the complex salt, tetra-ammine cupric sulphate $[Cu(NH_3)_4]SO_4$.

$$2CuSO_4 + 2NH_4OH = CuSO_4,Cu(OH)_2 + (NH_4)_2SO_4 ;$$
$$CuSO_4,Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH$$
$$= 2[Cu(NH_3)_4]SO_4 + 8H_2O.$$

4. **Potassium Ferrocyanide Solution** : reddish-brown precipitate of cupric ferrocyanide $Cu_2[Fe(CN)_6]$ from neutral or acid solutions. It is insoluble in dilute acids, but dissolves in aqueous ammonium hydroxide forming a blue solution. The precipitate is decomposed by solutions of alkali hydroxides with the separation of blue cupric hydroxide.

$$2CuSO_4 + K_4[Fe(CN)_6] = Cu_2[Fe(CN)_6] + 2K_2SO_4.$$

5. **Potassium Cyanide Solution** (*highly poisonous*) : yellow precipitate of cupric cyanide $Cu(CN)_2$, which quickly decomposes into cuprous cyanide $Cu_2(CN)_2$ and cyanogen $(CN)_2$. The cuprous cyanide dissolves in excess of the reagent forming a colourless solution of a complex salt, potassium cuprocyanide $K_3[Cu(CN)_4]$, in which the concentration of copper ions is so small that it is insufficient to give a precipitate with hydrogen sulphide (distinction from cadmium) (for detailed explanation see Complex Ions, Section **I, 20**).

$$2CuSO_4 + 4KCN = 2Cu(CN)_2 + 2K_2SO_4 ;$$
$$2Cu(CN)_2 = (CN)_2 + Cu_2(CN)_2 ;$$
$$Cu_2(CN)_2 + 6KCN = 2K_3[Cu(CN)_4] \textit{ or } K_6[Cu_2(CN)_8].$$

6. **Potassium Iodide Solution** : cupric iodide CuI_2 is first precipitated ; this immediately decomposes into white cuprous iodide Cu_2I_2 and free iodine. The latter dissolves in the excess of the potassium iodide solution and colours the solution brown.

$$CuSO_4 + 2KI = CuI_2 + K_2SO_4 ;$$
$$2CuI_2 = Cu_2I_2 + I_2 ;$$
$$\text{or} \quad CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2.$$

7. **Potassium or Ammonium Thiocyanate Solution** : black precipitate of cupric thiocyanate $Cu(CNS)_2$, which passes slowly, or immediately upon adding sulphurous acid solution, into white cuprous thiocyanate $Cu_2(CNS)_2$. The latter is insoluble in water and in dilute sulphuric and hydrochloric acids.

$$CuSO_4 + 2NH_4CNS = Cu(CNS)_2 + (NH_4)_2SO_4.$$
$$2Cu(CNS)_2 + H_2SO_3 + H_2O = Cu_2(CNS)_2 + 2HCNS + H_2SO_4.$$

8. **Iron.**—If a clean iron nail or the blade of a pen-knife is immersed in a solution of a cupric salt, a red deposit of copper is obtained (see Electrode Potentials, Section **I, 29**) :

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

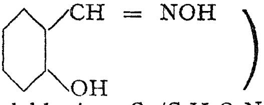
†*9.* **α-Benzoin Oxime (or Cupron) Reagent** ($C_6H_5.CHOH.C{=}NOH.C_6H_5$) : green precipitate of copper benzoin oxime $Cu(C_{14}H_{11}O_2N)$, insoluble in dilute ammonia solution. In the presence of metallic salts which are precipitated by ammonia solution, their precipitation can be prevented by the addition of sodium potassium tartrate. Large amounts of ammonium salts interfere and should be removed by evaporation and heating to glowing : the residue is then dissolved in a little dilute hydrochloric acid.

Treat some drop-reaction paper with a drop of the weakly acid test solution and a drop of the reagent, and then hold it over ammonia vapour. A green colouration is obtained.

Sensitivity : 0·1 μg. Cu. Concentration limit : 1 in 500,000.

If other ions, precipitable by ammonia solution, are present, a drop of 10 per cent Rochelle salt solution is placed upon the paper before the reagent is added.

The **reagent** is prepared by dissolving 5 g. of α-benzoin oxime in 100 c.c. of 95 per cent alcohol.

†*10.* **Salicylaldoxime Reagent** () : greenish-yellow precipitate of copper salicylaldoxime $Cu(C_7H_5O_2N)_2$ in acetic

acid solution, soluble in mineral acids. Only gold and palladium give precipitates in acetic acid solution and should therefore be absent.

Place a drop of the test solution, which has been neutralised and then acidified with acetic acid, in a micro test-tube and add a drop of the reagent. A yellow-green precipitate or opalescence (according to the amount of copper present) is obtained.

Sensitivity : 0·5 μg. Cu. Concentration limit : 1 in 100,000.

The **reagent** is prepared by dissolving 1 g. of salicylaldoxime in 5 c.c. of cold alcohol and pouring the solution dropwise into 95 c.c. of water at a temperature not exceeding 80°C ; the mixture is shaken until clear and filtered, if necessary.

†*11*. **Rubeanic Acid (or Dithio-oxamide) Reagent** $\{ (CS.NH_2)_2 \}$: black precipitate of copper rubeanate $Cu(CHNS)_2$ from ammoniacal or weakly acid solution. The precipitate is formed in the presence of alkali tartrates, but not in alkali-cyanide solutions. Only nickel and cobalt ions react under similar conditions yielding blue and brown precipitates respectively. Copper may, however, be detected in the presence of these elements by utilising the *capillary separation method* upon filter paper.

Place a drop of the neutral test solution upon drop-reaction paper, expose it to ammonia vapour and add a drop of the reagent. A black or greenish-black spot is produced.

Sensitivity : 0·01 μg. Cu. Concentration limit : I in 2,500,000.

Traces of copper in distilled water give a positive reaction, hence a blank test must be carried out with the distilled water.

In the **presence of nickel,** proceed as follows. Impregnate drop-reaction paper with the reagent and add a drop of the test solution acidified with acetic acid. Two zones or circles are formed : the central olive green or black ring is due to copper and the outer blue-violet ring to nickel.

Sensitivity : 0·05 μg. Cu in the presence of 20,000 times amount of Ni. Concentration limit : 1 in 1,000,000

In the **presence of cobalt,** the central green or black ring, due to copper, is surrounded by a yellow-brown ring of cobalt rubeanate.

Sensitivity : 0·25 μg. Cu in the presence of 2,000 times amount of Co. Concentration limit : 1 in 200,000.

The **reagent** consists of a 0·5 per cent solution of rubeanic acid in alcohol.

†*12*. **Ammonium Mercuri-thiocyanate Reagent** $\{ (NH_4)_2[Hg(CNS)_4] \}$: deep violet crystalline precipitate in the presence of zinc or cadmium ions. Cobalt and nickel interfere since they yield green or blue precipitates of the corresponding mercuri-thiocyanates $X[Hg(CNS)_4]$; the interference of ferric iron is avoided by carrying out the precipitation in the presence of alkali fluorides or oxalates.

Place a drop of the acid test solution upon a spot plate, add 1 drop of 1 per cent zinc acetate solution and 1 drop of the reagent. The precipitated zinc mercuri-thiocyanate is coloured violet.

Sensitivity : 0·1 μg. Cu. Concentration limit : 1 in 500,000.

(The addition of copper ions to a precipitate of zinc mercuri-thiocyanate, already formed, has no influence.)

The **reagent** is prepared by dissolving 9 g. of ammonium thiocyanate and 8 g. of mercuric chloride in 100 c.c. of water.

†*13.* **Catalytic Effect upon the Ferric Iron-Thiosulphate Reaction.**—Ferric salts react with thiosulphates in accordance with the equations:

$$Fe^{+++} + 2S_2O_3^{--} = [Fe(S_2O_3)_2]^- \text{ (violete complex ion)} \qquad (i);$$

$$[Fe(S_2O_3)_2]^- + Fe^{+++} = 2Fe^{++} + S_4O_6^{--} \qquad (ii).$$

Reaction (i) is fairly rapid; reaction (ii) is a slow one, but is enormously accelerated by traces of copper salts. If the reaction is carried out in the presence of a thiocyanate, which serves as an indicator for the presence of ferric iron and also retards reaction (ii), then the reaction velocity, which is proportional to the time taken for complete decolourisation, may be employed for detecting minute amounts of cupric ions.

Upon adjacent cavities of a spot plate place a drop of the test solution and a drop of distilled water. Add to each 1 drop of the ferric thiocyanate reagent and 3 drops of 0·1*N*-sodium thiosulphate solution. The decolourisation of the copper-free solution is complete in 1·5–2 minutes: if the test solution contains 1 μg. of copper, the decolourisation is instantaneous. For smaller amounts of copper, the difference in times between the two tests is still appreciable.

Sensitivity: 0·02 μg. Cu. Concentration limit: 1 in 2,500,000.

The **ferric thiocyanate reagent** is prepared by dissolving 1·5 g. of ferric chloride and 2·0 g. of potassium thiocyanate in 100 c.c. of water.

Dry Tests

(i) *Blowpipe test.*—When copper compounds are heated with alkali carbonate upon charcoal, red metallic copper is obtained, but no oxide is visible.

(ii) *Borax bead.*—Green while hot and blue when cold after heating in the oxidising flame; red in the reducing flame, best obtained by the addition of a trace of tin or by moistening with stannous chloride solution.

(iii) *Flame test.* Green especially in the presence of halides, *e.g.*, by moistening with concentrated hydrochloric acid before heating.

CADMIUM, Cd

Cadmium is a silver-white, malleable and ductile metal. It dissolves slowly in dilute hydrochloric and sulphuric acids with the evolution of hydrogen. The best solvent for the metal is nitric acid. Only one series of salts, derived from the oxide CdO, is of importance in qualitative analysis.

III, 9. REACTIONS OF THE CADMIUM ION, Cd^{++}

Use a solution of cadmium sulphate, $3CdSO_4,8H_2O$.

1. **Hydrogen Sulphide**: yellow precipitate of cadmium sulphide CdS from solutions acidified with a *little* hydrochloric acid (strength approximately 0·25 molar). The precipitate is soluble in hot dilute nitric acid and in hot dilute sulphuric acid (distinction from copper), but is insoluble in potassium cyanide solution (difference from copper). No precipitation takes place in strongly acid solutions owing to the reversibility of the reaction :

$$CdSO_4 + H_2S \rightleftharpoons CdS + H_2SO_4$$

(for a detailed discussion of the reaction see Section **I, 16**).

2. **Sodium Hydroxide Solution** : white precipitate of cadmium hydroxide $Cd(OH)_2$, insoluble in excess of the reagent.

$$CdSO_4 + 2NaOH = Cd(OH)_2 + Na_2SO_4.$$

3. **Ammonium Hydroxide Solution** : white precipitate of cadmium hydroxide, soluble in excess of the precipitant (distinction from lead and bismuth) ; the soluble complex salt, tetra-ammine cadmium sulphate $[Cd(NH_3)_4]SO_4$, is formed (see Complex Ions, Section **I, 20**).

$$CdSO_4 + 2NH_4OH = Cd(OH)_2 + (NH_4)_2SO_4 ;$$
$$Cd(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH = [Cd(NH_3)_4]SO_4 + 4H_2O.$$

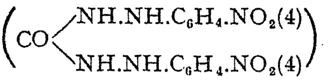
4. **Potassium Cyanide Solution** : white precipitate of cadmium cyanide $Cd\,CN)_2$, soluble in excess of the reagent to yield the complex, potassium cadmi-cyanide $K_2[Cd(CN)_4]$. A sufficiently high concentration of cadmium ions is produced by the dissociation of the complex ion to give a precipitate of yellow cadmium sulphide with hydrogen sulphide.

$$CdSO_4 + 2KCN = Cd(CN)_2 + K_2SO_4 ;$$
$$Cd(CN)_2 + 2KCN = K_2[Cd(CN)_4] ;$$
$$K_2[Cd(CN)_4] + H_2S = CdS + 2KCN + 2HCN.$$

The marked difference in the values of the instability constants of the complex ions $[Cd(CN)_4]^{--}$ and $[Cu(CN)_4]^{---}$ serves as the basis for one of the methods for the separation of copper and cadmium (for discussion, see Section **I, 20**).

5. **Ammonium Thiocyanate Solution** : no precipitate (distinction from copper).

†*6.* **Dinitro-diphenylcarbazide Reagent**



$$\left(CO\begin{matrix}\diagup NH.NH.C_6H_4.NO_2(4)\\ \diagdown NH.NH.C_6H_4.NO_2(4)\end{matrix}\right)$$

Cadmium hydroxide is coloured brown by the reagent, which rapidly becomes greenish-blue with formaldehyde.

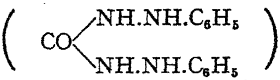
Place a drop of the acid, neutral or ammoniacal test solution on a spot plate and mix it with a drop of 10 per cent sodium hydroxide solution and 1 drop of 10 per cent potassium cyanide solution. Introduce 1 drop of the reagent and 2 drops of 40 per cent formaldehyde solution.

A brown precipitate is formed, which very rapidly becomes greenish-blue. The reagent alone is red in alkaline solution and is coloured violet with formaldehyde, hence it is advisable to compare the colour produced in a blank test with pure water when searching for minute amounts of cadmium.

Sensitivity: 0·8 μg. Cd. Concentration limit: 1 in 60,000.

In the presence of considerable amounts of copper, 3 drops each of the potassium cyanide and formaldehyde solution should be used; the sensitivity is 4 μg. Cd in the presence of 400 times the amount of Cu.

The **reagent** consists of a 0·1 per cent solution of dinitro-diphenylcarbazide in alcohol.

†7. **Diphenylcarbazide Reagent**  $\left(CO\begin{array}{l} \diagup NH.NH.C_6H_5 \\ \diagdown NH.NH.C_6H_5 \end{array} \right)$: violet precipitate or colouration in neutral or acetate-buffered solution.

Moisten some drop-reaction paper with the reagent and dry it. Place a drop of the test solution upon it and hold it over an open ammonia solution bottle for 1–2 minutes. A blue-violet colouration develops.

Sensitivity: 4 μg. Cd. Concentration limit: 1 in 12,500.

The **reagent** consists of a cold saturated solution of diphenylcarbazide in alcohol.

The reagent is far from specific for cadmium, but by further saturating the above reagent with solid potassium thiocyanate and adding a few crystals of potassium iodide, it can be used in the presence of copper, lead and mercury. The sensitivity of the modified reagent is about 8 μg. Cd. Magnesium also gives the reaction.

III, 10. Table XVIII.—Analysis of the Copper Group (Group IIA).

The ppt. obtained with H_2S in the presence of dilute HCl may contain the sulphides HgS, PbS, Bi_2S_3, CuS, CdS, and also SnS, SnS_2, As_2S_3 and Sb_2S_3. Pierce the point of the filter with a small glass rod, wash the ppt. into a beaker with a small quantity of water. Add 10 c.c. of yellow ammonium sulphide solution, heat to 50–60° for 2–3 minutes, filter and wash residue.

<table>
<tr>
<td colspan="4">Residue. May contain HgS, PbS, Bi_2S_3, CdS, CuS. Transfer ppt. to a beaker, add <i>ca.</i> 10 c.c. of dilute nitric acid (1 vol. acid to 2 vols. water), boil for a few minutes, filter and wash.</td>
<td rowspan="4">Filtrate. May contain metals of Group IIB.
(See Table XIX.)</td>
</tr>
<tr>
<td rowspan="3">Residue. Black; HgS. Dissolve in aqua regia or in concentrated hydrochloric acid + a little $KClO_3$: boil, dilute, add $SnCl_2$ solution. White or grey ppt.
Hg present.</td>
<td colspan="3">Filtrate. May contain $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$. Test a small portion for Pb by adding dilute H_2SO_4 and alcohol; white ppt. indicates Pb. If present, add dilute H_2SO_4 and concentrate in the fume chamber until thick white fumes appear. Cool, dilute and filter.</td>
</tr>
<tr>
<td rowspan="2">Residue. White; $PbSO_4$. Dissolve in ammonium acetate solution, add dilute acetic acid and K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$.
Pb present.</td>
<td colspan="2">Filtrate. May contain Bi^{+++}, Cu^{++}, Cd^{++}. Add ammonia solution in excess, filter.</td>
</tr>
<tr>
<td>Residue. White; $Bi(OH)_3$. Wash well, pour sodium stannite solution on filter. Blackening of ppt. Alternatively, dissolve the white precipitate in dilute HNO_3, and add Na_2HPO_4 solution. White ppt. of $BiPO_4$
Bi present.</td>
<td>Filtrate. May contain $[Cu(NH_3)_4]SO_4$ and $[Cd(NH_3)_4]SO_4$. If colourless, Cu absent; test then directly for Cd (see below). If blue, Cu present. If in doubt, add $K_4[Fe(CN)_6]$ solution and acetic acid; reddish-brown ppt. confirms Cu. Add KCN solution drop by drop until solution is decolourised, and test with a few bubbles of H_2S. Yellow ppt. of CdS.
Cd present.</td>
</tr>
</table>

III, 10. Table XVIIIA.—Analysis of the Copper Group (Group IIA).

The ppt. obtained with H_2S in the presence of dilute HCl may contain the sulphides HgS, PbS, Bi_2S_3, CuS, CdS, and also As_2S_3, Sb_2S_3, SnS and SnS_2. Pierce the point of the filter with a small glass rod, wash the ppt. into a beaker with a small quantity of water. Add 5–10 c.c. of yellow ammonium sulphide solution, heat to 50–60° for 2–3 minutes, filter and wash residue.

<table>
<tr><td colspan="4">Residue. May contain HgS, PbS, Bi_2S_3, CdS and CuS. Transfer to a small beaker, add <i>ca.</i> 10 c.c. of dilute nitric acid, boil gently for a few minutes, filter and wash.</td><td rowspan="4">Filtrate. May contain metals of Group IIB. (See Table XIX.)</td></tr>
<tr><td rowspan="3">Residue. Black; HgS. Dissolve in a mixture of 2·5 c.c. of 10% NaOCl solution and 0·5 c.c. of dilute HCl. Add 1 c.c. of dilute HCl, boil off excess of Cl_2 and cool. Add $SnCl_2$ solution White ppt., turning grey or black.
Hg (ic) present.</td><td colspan="3">Filtrate. May contain $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$. Add excess of concentrated NH_4OH solution until precipitation is complete. Filter.</td></tr>
<tr><td colspan="2">Residue. May contain $Bi(OH)_3$ and $Pb(OH)_2$. Warm with 5 c.c. of NaOH solution and filter.</td><td rowspan="2">Filtrate. May contain $[Cu(NH_3)_4]SO_4$ and $[Cd(NH_3)_4]SO_4$. If colourless, Cu is absent; test then directly for Cd by passing H_2S for 10–20 seconds into the ammoniacal solution. Yellow ppt. (CdS.)
Cd present.
If blue, Cu present. Divide solution into 2 unequal parts.
<i>Smaller portion.</i> Acidify with acetic acid and add $K_4[Fe(CN)_6]$ solution. Reddish-brown ppt.
Cu present.
<i>Larger portion.</i> Add KCN solution drop-wise until solution is decolourised. Pass H_2S for 30 seconds. Immediate yellow ppt. of CdS.
Cd present.</td></tr>
<tr><td>Residue. May be $Bi(OH)_3$. Wash. Pour sodium stannite solution on filter. Blackening of ppt.
Bi present.</td><td>Filtrate. May contain sodium plumbite Na_2PbO_2. Acidify with dilute acetic acid and add K_2CrO_4 solution. Yellow ppt. ($PbCrO_4$).
Pb present.</td></tr>
</table>

Dry Test

Blowpipe test.—All cadmium compounds when heated with alkali carbonate on charcoal give a brown incrustation of cadmium oxide CdO.

DETECTION AND SEPARATION OF THE METALS IN THE COPPER GROUP (GROUP IIA).

The foregoing reactions of the metals of the copper group furnish the facts upon which the table of separation is based [Table XVIII]. The student should use the test solution provided, or else prepare a solution of the chlorides of the metals and work through the table. The sulphides of the metals of this group, and also those of arsenic, antimony and tin (Group IIB), are precipitated by hydrogen sulphide in the presence of dilute hydrochloric acid. The reactions of the Group IIB metals will be studied later, but for the present it will suffice to state that the sulphides of the Group IIA metals are best separated from those of Group IIB by the solubility of the latter in warm yellow ammonium sulphide solution.

THE ARSENIC GROUP (GROUP IIB)

ARSENIC, As

Arsenic is a steel-grey, brittle solid with a metallic lustre. It sublimes on heating, and a characteristic, garlic-like odour is apparent; on heating in a free supply of air, arsenic burns with a blue flame yielding white fumes of arsenious oxide As_4O_6. *All arsenic compounds are poisonous.* The element is insoluble in hydrochloric acid and in dilute sulphuric acid: it dissolves readily in dilute nitric acid yielding arsenious oxide, and in concentrated nitric acid or in aqua regia or in sodium hypochlorite solution forming arsenic acid.

$$As_4 + 4HNO_3\ (\textit{dil.}) = As_4O_6 + 4NO + 2H_2O.$$

$$3As_4 + 20HNO_3\ (\textit{conc.}) + 8H_2O = 20NO + 12H_3AsO_4.$$

$$As_4 + 10NaOCl + 6H_2O = 4H_3AsO_4 + 10NaCl.$$

Two series of compounds of arsenic are commonly encountered: (*a*) The *arsenious* compounds are derived from the amphoteric arsenious oxide As_4O_6, which yields salts with strong acids, *e.g.*, arsenious chloride $AsCl_3$, and with strong bases, *e.g.*, sodium arsenite Na_3AsO_3. (*b*) The *arsenic* compounds corresponding to the pentoxide As_2O_5; they are usually salts of the tribasic orthoarsenic acid, *e.g.*, Na_2HAsO_4, NaH_2AsO_4 and Na_3AsO_4.

III, 11. REACTIONS OF ARSENIOUS COMPOUNDS

Use a solution of arsenious oxide * in hydrochloric acid, or a solution of sodium arsenite, Na_3AsO_3.

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* Arsenious oxide is sparingly soluble in water yielding a solution containing the weak arsenious acid; the oxide, however, is recovered upon concentrating the solution.

$$As_4O_6 + 6H_2O \rightleftharpoons 4H_3AsO_3.$$

1. **Hydrogen sulphide**: yellow precipitate of arsenious sulphide As_2S_3 in acid (hydrochloric) solution.

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O;$$

$$2AsCl_3 + 3H_2S \rightleftharpoons As_2S_3 + 6HCl;$$

$$2Na_3AsO_3 + 6HCl + 3H_2S = As_2S_3 + 6NaCl + 6H_2O.$$

The precipitate is insoluble in hot concentrated hydrochloric acid (distinction and method of separation from Sb_2S_3 and SnS_2), but dissolves in hot concentrated nitric acid:

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO;$$

it is readily soluble in solutions of alkali hydroxides, ammonium sulphide and ammonium carbonate (the last reaction distinguishes it from Sb_2S_3 and SnS_2).

$$As_2S_3 + 6NaOH = 3H_2O + Na_3AsO_3 + Na_3AsS_3 \text{ (sodium thioarsenite)};$$

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3;$$

$$As_2S_3 + 3(NH_4)_2CO_3 = 3CO_2 + (NH_4)_3AsO_3 + (NH_4)_3AsS_3.$$

Upon acidifying any of the above solutions thioarsenious acid, H_3AsS_3, is set free; this acid does not exist in the free state, but decomposes immediately into arsenious sulphide and hydrogen sulphide. Hence on treating a mixture of arsenite and thioarsenite with dilute hydrochloric acid, arsenious sulphide is precipitated.

$$2(NH_4)_3AsS_3 + 6HCl = 6NH_4Cl + 2H_3AsS_3;$$

$$2H_3AsS_3 = As_2S_3 + 3H_2S;$$

$$(NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2O.$$

The formation of soluble thio-salts explains the non-precipitation of arsenious sulphide from solutions of arsenites in neutral or alkaline solution; for complete precipitation of arsenic as the trisulphide, sufficient free acid must be present in the solution to prevent the formation of soluble thio-salts:

$$Na_3AsO_3 + 3H_2S \rightleftharpoons Na_3AsS_3 + 3H_2O.$$

Arsenious sulphide dissolves readily in yellow ammonium sulphide solution $(NH_4)_2S_x$ forming first ammonium thioarsenite $(NH_4)_3AsS_3$, which is then oxidised to the thioarsenate $(NH_4)_3AsS_4$ by excess of sulphur. Upon acidifying the solution arsenic pentasulphide As_2S_5 is precipitated, together with a little sulphur, produced by the decomposition of the excess of the ammonium polysulphide by the acid.

$$As_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3AsS_4 + S;$$
$$2(NH_4)_3AsS_4 + 6HCl = 3H_2S + As_2S_5 + 6NH_4Cl.$$

2. **Silver Nitrate Solution**: yellow precipitate of silver arsenite Ag_3AsO_3 from *neutral* solutions (distinction from arsenates), soluble in ammonium hydroxide solution and in nitric acid (compare Section **I, 19**).

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3.$$

3. **Magnesia Mixture** (a solution containing $MgCl_2$, NH_4OH and NH_4Cl): no precipitate (distinction from arsenate).

The *reagent* is prepared by dissolving 50 g. of $MgCl_2,6H_2O$, 50 g. of NH_4Cl in water, adding 25 c.c. of ammonia solution (sp. gr. 0·88), and diluting to 500 c.c.

4. **Copper Sulphate Solution**: green precipitate of copper arsenite (Scheele's green), variously formulated as $CuHAsO_3$ and $Cu_3(AsO_3)_2,xH_2O$, from neutral solutions, soluble in acids, and also in ammonium hydroxide solution forming a blue solution.

5. **Solution of Iodine in Potassium Iodide Solution**: decolourised, owing to the formation of hydriodic and arsenic acids.

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

The reaction is not a quantitative one because of the reducing character of the hydrogen iodide formed; in the presence of excess of sodium bicarbonate solution, which neutralises the hydriodic acid as formed, the reaction is quantitative. Sodium carbonate cannot be employed as this reacts with the iodine.

$$Na_3AsO_3 + I_2 + 2NaHCO_3 = Na_3AsO_4 + 2NaI + 2CO_2 + H_2O.$$
$$3Na_2CO_3 + 3I_2 = NaIO_3 + 5NaI + 3CO_2.$$

6. **Stannous Chloride Solution and Concentrated Hydrochloric Acid (Bettendorff's Test).**—A few drops of the arsenite solution are added to 4 c.c. of concentrated hydrochloric acid and 1 c.c. of saturated stannous chloride solution, and the solution gently warmed; the solution becomes dark brown and finally black, due to the separation of metallic arsenic.

$$Na_3AsO_3 + 6HCl = AsCl_3 + 3NaCl + 3H_2O;$$
$$2AsCl_3 + 3SnCl_2 = 2As + 3SnCl_4.$$

If the test be made with the sulphide precipitated in acid solution, then only mercury will interfere; this is best removed by converting into magnesium ammonium arsenate and glowing, when the pyroarsenate $Mg_2As_2O_7$ remains. This forms the basis of a delicate test for arsenious and arsenic arsenic.

† Mix a drop of the test solution in a micro-crucible with 1–2 drops of concentrated ammonia solution, 2 drops of " 20-volume " hydrogen peroxide, and 2 drops of 10 per cent magnesium chloride solution. Evaporate slowly and finally heat until fuming ceases. Treat the residue with 1–2 drops of a solution of stannous chloride in concentrated hydrochloric acid, and warm slightly. A brown or black precipitate or colouration is obtained.

Sensitivity: 1 μg. As. Concentration limit: 1 in 50,000.

III, 12. REACTIONS OF ARSENIC COMPOUNDS.

Use a solution of sodium arsenate, $Na_2HAsO_4,12H_2O$ or a solution of arsenic pentoxide As_2O_5, containing some dilute hydrochloric acid.

1. **Hydrogen Sulphide**: no immediate precipitate in the presence of dilute hydrochloric acid. If the passage of the gas is continued, a mixture of arsenious sulphide As_2S_3 and sulphur is slowly precipitated. Precipitation is more rapid in hot solution.

$$H_3AsO_4 + H_2S = H_2O + H_3AsO_3S \text{ (thioarsenic acid) ;}$$
$$H_3AsO_3S = S + H_3AsO_3 \text{ (arsenious acid) ;}$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

If a large excess of concentrated hydrochloric acid is present and hydrogen sulphide is passed rapidly into the cold solution, yellow arsenic pentasulphide As_2S_5 is precipitated; in the hot solution, the precipitate consists of a mixture of the tri- and penta-sulphides.

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O.$$

Arsenic pentasulphide, like the trisulphide, is readily soluble in solutions of caustic alkalis, ammonium sulphide or polysulphide and ammonium carbonate, but is insoluble in boiling concentrated hydrochloric acid:

$$As_2S_5 + 6NaOH = 3H_2O + Na_3AsS_4 + Na_3AsO_3S\ ;$$
$$As_2S_5 + 3(NH_4)_2CO_3 = 3CO_2 + (NH_4)_3AsS_4 + (NH_4)_3AsO_3S;$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

Upon acidifying these solutions with hydrochloric acid, arsenic pentasulphide is precipitated:

$$2(NH_4)_3AsS_4 + 6HCl = 3H_2S + As_2S_5 + 6NH_4Cl.$$

For the rapid precipitation of arsenic from solutions of arsenates without using a large excess of hydrochloric acid, sulphur dioxide may be passed into the slightly acid solution in order to reduce the arsenic to the tervalent state and then the excess of sulphur dioxide is boiled off ; upon conducting hydrogen sulphide into the warm reduced solution, immediate precipitation of arsenic trisulphide occurs :

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4.$$

The precipitation can be greatly accelerated by the addition of small amounts of an iodide, say, 1 c.c. of a 10 per cent solution, and a little concentrated hydrochloric acid. The iodide acts as a catalyst in that it reduces the arsenic acid thus :

$$2AsO_4^{---} + 4I^- + 4H^+ \rightleftharpoons 2AsO_3^{---} + 2I_2 + 2H_2O,$$

and the iodine liberated is converted into iodide ions by the hydrogen sulphide :

$$2I_2 + 2H_2S \rightleftharpoons 4HI + 2S.$$

2. **Silver Nitrate Solution** : chocolate brown precipitate of silver arsenate Ag_3AsO_4 from neutral solutions (distinction from arsenite and phosphate which yield yellow precipitates), soluble in acids and in ammonium hydroxide solution but insoluble in acetic acid.

$$Na_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3NaNO_3,$$

† This reaction may be adapted as a delicate test for arsenic in the following manner. The test is applicable only in the absence of chromates, ferro- and ferri-cyanides, which also give coloured silver salts insoluble in acetic acid.

Place a drop of the test solution in a micro-crucible, add a few drops of concentrated ammonia solution and of " 20-volume " hydrogen peroxide, and warm. Acidify with acetic acid and add 2 drops of 1 per cent silver nitrate solution. A red-brown precipitate or colouration appears.

Sensitivity : 6 μg. As. Concentration limit : 1 in 8,000.

3. **Magnesia Mixture** (a solution containing $MgCl_2$, NH_4OH and NH_4Cl) : white crystalline precipitate of magnesium ammonium arsenate $Mg(NH_4)AsO_4,6H_2O$ from neutral or ammoniacal solutions (distinction from arsenite).

$$Na_2HAsO_4 + MgCl_2 + NH_4OH = Mg(NH_4)AsO_4 + H_2O + 2NaCl.$$

Upon treating the white precipitate with silver nitrate solution containing a few drops of acetic acid, brown silver arsenate is formed (distinction from phosphate) :

$$Mg(NH_4)AsO_4 + 3AgNO_3 = Ag_3AsO_4 + Mg(NO_3)_2 + NH_4NO_3.$$

4. **Ammonium Molybdate Solution**.—When the reagent and nitric acid are added in considerable excess to a solution of an arsenate, a yellow crystalline precipitate of ammonium arsenomolybdate, $(NH_4)_3[AsMo_{12}O_{40}]$ is obtained on boiling (distinction from arsenites which give no precipitate, and from phosphates which yield a precipitate in the cold or upon gentle warming). The precipitate is insoluble in nitric acid, but dissolves in ammonium hydroxide solution and in solutions of caustic alkalis.

$$Na_2HAsO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = (NH_4)_3[AsMo_{12}O_{40}] + 21NH_4NO_3 + 2NaNO_3 + 12H_2O.$$

5. **Potassium Iodide Solution**: in the presence of concentrated hydrochloric acid, iodine is precipitated; upon shaking the mixture with 1–2 c.c. of chloroform the latter is coloured blue by the iodine. The reaction may be used for the *detection of arsenate in the presence of arsenite*; oxidising agents must be absent.

$$H_3AsO_4 + 2HI \rightleftharpoons H_3AsO_3 + I_2 + H_2O.$$

6. **Uranyl Acetate Solution**: light yellow, gelatinous precipitate of uranyl ammonium arsenate $UO_2(NH_4)AsO_4, xH_2O$ in the presence of excess of ammonium acetate, soluble in mineral acids but insoluble in acetic acid. If precipitation is carried out from a hot solution of an arsenate, the precipitate is obtained in granular form. This test provides an excellent method of distinction from arsenites, which do not give a precipitate with the reagent (an approximately $0{\cdot}1N$ solution of uranyl acetate).

$$Na_2HAsO_4 + UO_2(C_2H_3O_2)_2 + NH_4OH = UO_2(NH_4)AsO_4 + 2Na.C_2H_3O_2 + H_2O$$

III, 13. SPECIAL TESTS FOR SMALL AMOUNTS OF ARSENIC

The following tests are applicable to *all* arsenic compounds.

(i) **Marsh's Test.**—This test, which must be carried out in the fume chamber, is based upon the fact that all soluble compounds of arsenic are reduced by "nascent" hydrogen in acid solution to arsine AsH_3, a colourless, extremely poisonous gas with a garlic-like odour. If the gas, mixed with hydrogen, be conducted through a heated glass tube, it is decomposed into hydrogen and metallic arsenic, which is deposited as a brownish-black "mirror" just beyond the heated part of the tube.

On igniting the mixed gases, composed of hydrogen and arsine (after all the air has been expelled from the apparatus), they burn with a livid blue flame, and white fumes of arsenious oxide are evolved; if the inside of a small porcelain dish be pressed down upon the flame, a black deposit of arsenic is obtained on the cool surface, and the deposit is readily soluble in sodium hypochlorite or bleaching powder solution (distinction from antimony).

$$As_4O_6 + 12Zn + 12H_2SO_4 = 4AsH_3 + 12ZnSO_4 + 6H_2O.$$
$$H_3AsO_4 + 4Zn + 4H_2SO_4 = AsH_3 + 4ZnSO_4 + 4H_2O.$$
$$4AsH_3 = As_4 + 6H_2 \text{ (heat)}.$$
$$4AsH_3 + 6O_2 = As_4O_6 + 6H_2O.$$
$$As_4 + 10NaOCl + 6H_2O = 4H_3AsO_4 + 10NaCl.$$

The Marsh test is best carried out as follows. The apparatus is fitted up as shown in Fig. 41. A conical flask of about 125 c.c. capacity is fitted with a two-holed rubber stopper carrying a thistle funnel reaching nearly to the bottom of the flask and a 5-7 mm. right-angle tube; the latter is attached by a short piece of "pressure" tubing to a U-tube filled with glass wool moistened with lead acetate solution to absorb any hydrogen sulphide evolved (this may be dispensed with, if desired, as its efficacy has been questioned), then to a small tube containing anhydrous calcium chloride of about 8 mesh, then to a hard glass tube, *ca.* 25 cm. long and 7 mm, diameter, constricted twice near the middle to about 2 mm. diameter. the distance between the constrictions being 6-8 cms. The drying tubes and the tube *ABC* are securely supported by means of clamps. All reagents must be arsenic-free. Place 15-20 grams of arsenic-free zinc in the flask, add dilute sulphuric acid (1 : 3) until hydrogen is vigorously evolved. The purity of the reagents is tested by passing the gases, by means of a delivery tube attached by a short piece

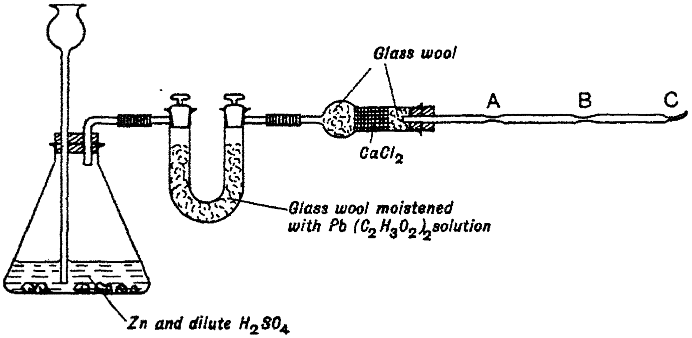


Fig. 41.

of rubber tubing to the end of *C*, through silver nitrate solution for several minutes ; the absence of a black precipitate or suspension proves that appreciable quantities of arsenic are not present.

$$6AgNO_3 + 3H_2O + AsH_3 = H_3AsO_3 + 6Ag + 6HNO_3.$$

The solution containing the arsenic compound is then added in small amounts at a time to the contents of the flask. If much arsenic is present, there will be an almost immediate blackening of the silver nitrate solution. Disconnect the rubber tube at *C*. Heat the tube at *A* to just below the softening point ; a mirror of arsenic is deposited in the cooler, less constricted portion of the tube. A second flame may be applied at B to ensure complete decomposition (arsine is extremely poisonous). When a satisfactory mirror has been obtained, remove the flames at A and B and apply a light at *C*. Hold a cold porcelain dish in the flame, and test the solubility of the black or brownish deposit in sodium hypochlorite solution.

The arsenic in the silver nitrate solution is present as arsenious acid and can be detected by the usual tests, *e.g.*, by hydrogen sulphide after removing the excess of silver nitrate with dilute hydrochloric acid, or by neutralising and adding further silver nitrate solution, if necessary.

The original Marsh test involved burning and deposition of the arsenic upon a cold surface. Nowadays the mirror test is usually applied. The silver nitrate reaction (sometimes known as Hofmann's test) is very useful as a confirmatory test.

(ii) **Gutzeit's Test.**—This is essentially a modification of Marsh's test, the chief difference being that only a test-tube is required and the arsine is detected by means of silver nitrate or mercuric chloride. Place 1-2 grams of arsenic-free zinc in a test-tube, add 5-7 c.c. of dilute sulphuric acid, loosely plug the tube with purified cotton wool and then place a piece of filter paper moistened with silver nitrate solution on top of the tube (Fig. 42). It may be necessary to warm the tube gently to produce a regular evolution of hydrogen. At the end of a definite period, say 2 minutes, remove the filter paper and examine the part that covered the test-tube ; usually a light-brown spot is obtained owing to the traces of arsenic present in the reagents. Remove the cotton wool plug, add 1 c.c. of the solution to be tested, replace the cotton-wool and silver nitrate paper, the latter displaced so that a fresh portion is exposed. After 2 minutes, assuming that the rate of evolution of gas is

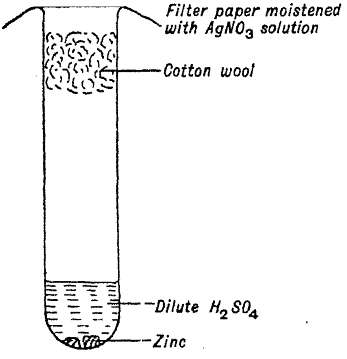


Fig. 42

approximately the same, remove the filter paper and examine the two spots. If much arsenic is present, the second spot (due to metallic silver), will appear black.

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + 6HNO_3 + H_3AsO_3.$$

Hydrogen sulphide, phosphine PH_3 and stibine SbH_3 give a similar reaction. They may be removed by means of a purified cotton wool plug impregnated with cuprous chloride.

The use of **mercuric chloride paper,** prepared by immersing filter paper in a 5 per cent solution of mercuric chloride in alcohol and drying in the atmosphere out of contact with direct sunlight, constitutes an improvement. This is turned yellow by a little arsine and reddish-brown by larger quantities. Filter paper, impregnated with 1 per cent aqueous solution of " gold chloride " $HAuCl_4,2H_2O$, may also be employed when a dark-red to blue-red stain is produced. A blank test must be performed with the reagent in all cases.

(iii) **Fleitmann's Test.**—This test depends upon the fact that nascent hydrogen generated in alkaline solution, *e.g.*, from aluminium or zinc and sodium hydroxide solution, reduces arsenious compounds to arsine, but does not affect antimony compounds. A method of distinguishing arsenic and antimony compounds is thus provided. Arsenates must first be reduced to the arsenious condition before applying the test. The *modus operandi* is as for the Gutzeit test, except that zinc or aluminium and sodium hydroxide solution replace zinc and dilute sulphuric acid. It is necessary to warm the solution. A black stain of silver is produced by the action of the arsine.

(iv) **Reinsch's Test.**—If a strip of bright copper foil be boiled with a solution of an arsenious compound acidified with at least one tenth of its bulk of concentrated hydrochloric acid, the arsenic is deposited upon the copper as a grey film of copper arsenide Cu_5As_2. Antimony, mercury, silver and other metals are precipitated under similar conditions. It is therefore necessary to test for arsenic in the deposit in the dry way. The strip is washed with distilled water, dried between filter paper and then gently heated in a test-tube; a white crystalline deposit of arsenious oxide is obtained. The latter is identified by examination with a hand lens, when it will be seen to consist of colourless octahedral and tetrahedral crystals; it may also be dissolved in water and tested for arsenic by Fleitmann's or Bettendorff's test.

Arsenates are also reduced by copper, but only slowly even on boiling.

Dry Tests

(i) *Blowpipe test.*—Arsenic compounds when heated upon charcoal with sodium carbonate give a white incrustation of arsenious oxide, and an odour of garlic is apparent while hot.

(ii) When heated with excess of potassium cyanide and of anhydrous sodium carbonate in a dry bulb tube, a black mirror of arsenic, soluble in sodium hypochlorite solution, is produced in the cooler part of the tube.

ANTIMONY, Sb

Antimony is a lustrous, silver-white metal. It is insoluble in hydrochloric acid and in dilute sulphuric acid, is slowly attacked by hot concentrated sulphuric acid yielding unstable antimonious sulphate, and is converted into antimony tri- or pentoxide by nitric acid, depending upon the amount and the concentration of the acid. The best solvent for antimony is aqua regia ; a solution of antimony tri- or penta-chloride is formed.

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 6H_2O + 3SO_2.$$

$$4Sb + 4HNO_3 = Sb_4O_6 + 4NO + 2H_2O.$$

$$6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O.$$

$$Sb + HNO_3 + 3HCl = SbCl_3 + NO + 2H_2O.$$

Two series of salts are known, the antimonious and antimonic corresponding respectively to the oxides Sb_4O_6 and Sb_2O_5, the former being the more important. Antimonious compounds react with water similarly to bismuth salts forming compounds containing the antimonyl group SbO— (compare Hydrolysis of Salts, Section **I, 40**).

$$SbCl_3 + H_2O \rightleftharpoons SbO.Cl + 2HCl.$$

An important antimonyl compound is tartar emetic, potassium antimonyl tartrate $K(SbO).C_4H_4O_6,0{\cdot}5H_2O$; it is prepared by the interaction between antimonious oxide and potassium hydrogen tartrate.

$$Sb_4O_6 + 4KH.C_4H_4O_6 = 4K(SbO).C_4H_4O_6 + 2H_2O.$$

The solubility of antimonyl compounds in solutions of tartaric acid or of tartrates is due to the formation of compounds of this type. The addition of dilute hydrochloric acid to an aqueous solution of tartar emetic gives a white precipitate of antimonyl chloride, soluble in excess of acid :

$$K(SbO).C_4H_4O_6 + 2HCl = H_2C_4H_4O_6 + SbO.Cl + KCl.$$

III, 14. REACTIONS OF ANTIMONIOUS COMPOUNDS

Use a solution of antimony trichloride, $SbCl_3$, prepared by dissolving either the solid trichloride or antimonious oxide, Sb_4O_6, in dilute hydrochloric acid.

1. **Hydrogen Sulphide** : orange-red precipitate of antimony trisulphide Sb_2S_3 from solutions which are not too acid. The precipitate is soluble in warm concentrated hydrochloric acid (distinction from arsenious sulphide), in ammonium polysulphide forming salts of thioantimonic acid H_3SbS_4, but is insoluble in ammonium carbonate solution.

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl;$$
$$Sb_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S.$$

Upon acidifying the solution of the thio-salt with hydrochloric acid, the orange antimony pentasulphide Sb_2S_5 is precipitated:

$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S.$$

2. **Water.**—When the solution is poured into water, a white precipitate of antimonyl chloride SbO.Cl is formed, soluble in hydrochloric acid and in tartaric acid solution (difference from bismuth). With a large excess of water the hydrated oxide Sb_4O_6,xH_2O is produced.

3. **Sodium Hydroxide or Ammonium Hydroxide Solution**: white precipitate of the hydrated antimonious oxide Sb_4O_6,xH_2O, soluble in concentrated solutions of caustic alkalis forming antimonites.

$$4SbCl_3 + 12NaOH = Sb_4O_6 + 12NaCl + 6H_2O;$$
$$Sb_4O_6 + 4NaOH = 4Na[SbO_2] + 2H_2O.$$

4. **Zinc**: a black precipitate of antimony is produced. If some of the antimony trichloride solution is poured upon some platinum foil and a piece of metallic zinc be placed on the foil, a black stain of antimony is formed upon the platinum; the stain (or deposit) should be dissolved in a little warm dilute nitric acid and hydrogen sulphide passed into the solution after dilution; an orange precipitate of antimony trisulphide will be obtained.

$$2SbCl_3 + 3Zn = 2Sb + 3ZnCl_2.$$

Some stibine SbH_3 may be evolved with the zinc; it is preferable to use tin.

A modification of the above test is to place a drop of the solution containing antimony upon a silver coin and to touch the coin through the drop with a piece of tin or zinc; a black spot will form on the coin.

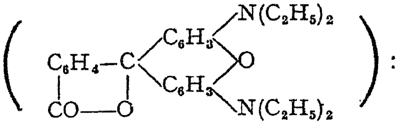
5. **Iron Wire**: black precipitate of antimony. This may be confirmed as described in reaction *4*.

6. **Potassium Iodide Solution**: yellow colouration owing to the formation of a complex salt.

7. **Cupferron Reagent***: yellowish-white precipitate.

* For further details of this reagent, see Section **III, 20,** reaction *9*.

†*8*. **Rhodamine-B** (or **Tetraethyl-rhodamine**) **Reagent**



violet or blue colouration with quinquevalent antimony. Tervalent antimony does not respond to this test, hence it must be oxidised with potassium or sodium nitrite and concentrated hydrochloric acid. Tin and small quantities of iron do not interfere, but mercury, thallium, gold, molybdates and tungstates in acid solution give similar colour reactions.

The test solution should be strongly acid with hydrochloric acid and the antimonious antimony oxidised, if necessary, by the addition of a little sodium or potassium nitrite. Place 1 c.c. of the reagent on a spot plate, and add 1 drop of the test solution. The light red colour of the reagent changes to violet.

Sensitivity: 0·5 μg. Sb and applicable in the presence of 12,500 times the amount of Sn. Concentration limit: 1 in 100,000.

The **reagent** is prepared by dissolving 0·01 g. of rhodamine-B in 100 c.c. of water.

†*9*. **Phosphomolybdic Acid Reagent**: " molybdenum blue " is produced. Only stannous tin interferes with this test. If, however, the insoluble ammonium phosphomolybdate, prepared by exposing the impregnated test paper to ammonia vapour, is employed, antimonious salts have no effect but stannous salts yield " molybdenum blue."

The test solution may consist of the Group IIB (arsenic group) precipitated dissolved in 1:1-hydrochloric acid. Place a drop of the test solution upon drop-reaction paper which has been impregnated with the phosphomolybdic acid reagent and hold the paper in steam. A blue colouration appears within a few minutes.

Sensitivity: 0·2 μg. Sb. Concentration limit: 1 in 250,000.

The **reagent** consist of a 5 per cent aqueous solution of phosphomolybdic acid.

III, 15. REACTIONS OF ANTIMONIC COMPOUNDS

Use a solution of antimony pentoxide in concentrated hydrochloric acid, or of potassium antimonate, KH_2SbO_4.

$$Sb_2O_5 + 10HCl = 2SbCl_5 + 5H_2O.$$

1. **Hydrogen Sulphide**: orange-red precipitate of antimony pentasulphide Sb_2S_5 in moderately acid solutions. The precipitate is insoluble in ammonium carbonate solution, soluble in ammonium sulphide solution yielding a thioantimonate, and is also dissolved by concentrated hydrochloric acid with the formation of antimony trichloride and the separation of sulphur. The thio-salt is decomposed by acids, the pentasulphide being precipitated.

$$2SbCl_5 + 5H_2S = Sb_2S_5 + 10HCl;$$

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 2S + 3H_2S;$$

$$Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4;$$

$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S.$$

2. **Water** : white precipitate of basic salt.

3. **Potassium Iodide Solution** : iodine separates out from a hydrochloric acid solution (difference from antimonious compounds).

$$2SbCl_5 + 2KI = I_2 + 2SbCl_3 + 2KCl.$$

4. **Zinc or Tin** : black precipitate of antimony in the presence of hydrochloric acid (see antimonious compounds).

5. **Cupferron Reagent** : no precipitate (difference from antimonious compounds).

† *6.* **Rhodamine-B Reagent** : see under Antimonious Compounds.

SPECIAL TESTS FOR SMALL AMOUNTS OF ANTIMONY

(i) **Marsh's Test.**—This test is carried out exactly as described for arsenic. The stibine SbH_3 (mixed with hydrogen) which is evolved burns with a faintly bluish-green flame and produces a *dull* black spot upon a cold porcelain dish held in the flame ; this deposit is insoluble in sodium hypochlorite or bleaching powder solution, but is dissolved by a solution of tartaric acid (difference from arsenic).

The gas is also decomposed by passage through a tube heated to dull redness. A lustrous mirror of antimony is formed in a similar manner to the arsenic mirror, but it is deposited on *both* sides of the heated portion of the tube because of the greater instability of the stibine. This mirror may be converted into orange-red antimony trisulphide by dissolving it in a little boiling hydrochloric acid and passing hydrogen sulphide into the solution.

When the stibine-hydrogen mixture is passed into a solution of silver nitrate (Hofmann's test), a black precipitate of silver antimonide $SbAg_3$ is obtained ; this is decomposed by the excess of silver nitrate into silver and antimonious oxide :

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3;$$

$$4Ag_3Sb + 12AgNO_3 + 6H_2O = 24Ag + Sb_4O_6 + 12HNO_3.$$

It is best to dissolve the precipitate in a solution of tartaric acid and to test for antimony with hydrogen sulphide in the usual manner.

(ii) **Gutzeit's Test.**—A brown stain is produced which is soluble in 80% alcohol, provided the antimony concentration of the solution is not too high.

(iii) **Fleitmann's or Bettendorff's Tests.**—Negative results are obtained when these are applied to antimony compounds (distinction from arsenic).

(iv) **Reinsch's Test.**—A grey to black deposit is formed upon the copper. Ignition of this deposit in a dry test-tube gives a non-crystalline sublimate of antimonious oxide, soluble in potassium hydrogen tartrate solution ; hydrogen sulphide precipitates orange-red antimony sulphide from this solution, acidified with hydrochloric acid.

Dry Test

Blowpipe Test.—When antimony compounds are heated with sodium carbonate upon charcoal, a brittle metallic bead, surrounded by a white incrustation, is obtained.

TIN, Sn

Tin is a silver-white metal, which is malleable and ductile at ordinary temperatures, but at low temperatures it becomes brittle, due to transformation into an allotropic modification. The metal dissolves slowly in dilute hydrochloric and sulphuric acids with the liberation of hydrogen and the formation of stannous salts ; it is readily dissolved by the hot concentrated acids. Dilute nitric acid dissolves tin slowly without any evolution of gas, stannous nitrate and ammonium nitrate being formed ; with concentrated nitric acid, a vigorous reaction occurs, a white solid, usually formulated as hydrated stannic oxide SnO_2,xH_2O and sometimes known as metastannic acid, being produced. Solution takes place readily with aqua regia ; stannic chloride is the sole product.

$$Sn + 2HCl \text{ (dilute and conc.)} = SnCl_2 + H_2.$$
$$Sn + H_2SO_4 \text{ (dilute)} = SnSO_4 + H_2.$$
$$Sn + 4H_2SO_4 \text{ (conc.)} = Sn(SO_4)_2 + 2SO_2 + 4H_2O.$$
$$4Sn + 10HNO_3 \text{ (dilute)} = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$
$$3Sn + 4HNO_3 + (x-2)\, H_2O = 4NO + 3SnO_2,xH_2O.$$
$$3Sn + 4HNO_3 + 12HCl = 4NO + 3SnCl_4 + 8H_2O.$$

Tin forms two oxides : stannous oxide SnO and stannic oxide SnO_2 from which the stannous and stannic salts respectively are derived. Both oxides are amphoteric, the stannic compound to the greater degree.

III, 16. REACTIONS OF STANNOUS COMPOUNDS

Use a solution of stannous chloride, $SnCl_2,2H_2O$, in dilute hydrochloric acid.

1. **Hydrogen Sulphide**: brown precipitate of stannous sulphide SnS from not too acid solutions (say in the presence of 0·25–0·3M hydrochloric acid or $pH \ngtr 0{\cdot}6$ {compare Section **I, 37**}). The precipitate is soluble in concentrated hydrochloric acid (distinction from arsenious sulphide), soluble in yellow, but not in colourless, ammonium sulphide solution to form a thiostannate; it is insoluble in ammonium carbonate solution (distinction from arsenious sulphide). Treatment of the solution of ammonium thiostannate with an acid yields a yellow precipitate of *stannic* sulphide SnS_2.

$$SnCl_2 + H_2S = SnS + 2HCl;$$
$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3;$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

Stannous sulphide is practically insoluble in solutions of caustic alkalis; hence, if sodium or potassium hydroxide solutions are employed for separating Group IIA and Group IIB, the tin must be oxidised to the stannic state before precipitation with hydrogen sulphide.

2. **Sodium Hydroxide Solution**: white precipitate of stannous hydroxide, soluble in excess of alkali forming sodium stannite $Na_2[SnO_2]$.

$$SnCl_2 + 2NaOH = Sn(OH)_2 + 2NaCl;$$
$$Sn(OH)_2 + 2NaOH = Na_2[SnO_2] + 2H_2O.$$

With ammonium hydroxide solution, white stannous hydroxide is precipitated, but this is not appreciably soluble in excess of the reagent.

3. **Mercuric Chloride Solution**: white precipitate of mercurous chloride Hg_2Cl_2. If the stannous chloride solution is present in excess, the precipitate turns grey, especially on warming, owing to further reduction to metallic mercury.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2;$$
$$SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg.$$

4. **Bismuth Nitrate Solution and Sodium Hydroxide Solution**: black precipitate of metallic bismuth (see under Bismuth, Section **III, 7,** reaction *5*).

5. **Metallic Zinc**: spongy tin is deposited which adheres to the zinc. If the zinc rests upon platinum foil, as described under antimony (Section **III, 14,** reaction *4*), and the solution is weakly acid, the tin is partially deposited upon the zinc in a spongy form but does not stain the platinum. The precipitate should be dissolved in concentrated hydrochloric acid and the mercuric chloride test applied.

6. **Cupferron Reagent**: white precipitate.

†*7.* **Dimethylglyoxime-Ferric Chloride Test.**—No colouration is produced when ferric salts are mixed with the dimethylglyoxime reagent and a little ammonia solution, but if a trace of ferrous iron is present, produced by reduction with stannous ions, a deep red colouration, due to ferrous dimethylglyoxime, is formed.

Mix a drop of the strongly acid stannous salt solution on a spot plate with 1 drop of 0·1*N*–ferric chloride solution acidified with hydrochloric acid, and after one minute add a minute crystal of tartaric acid (to prevent the formation of ferric hydroxide) and stir until dissolved. Add 1 drop of a 1 per cent solution of dimethylglyoxime in alcohol, followed by a drop of ammonia solution. A red colouration is produced.

Sensitivity: 0·05 μg. Sn. Concentration limit: 1 in 1,250,000.

†*8.* **Cacotheline Reagent** (a nitro-derivative of brucine): violet colouration with stannous salts. The following interfere with the test: coloured ions; silver, mercury, molybdenum, chromium, ferric iron, cobalt and nickel; titanous chloride; antimonious salts (slight); hyposulphites, sulphites, bisulphites and selenites. It is said that the addition of a little 2 per cent hydroxylamine hydrochloride solution eliminates the interference of a number of the above elements and radicals.

Impregnate some drop-reaction paper with the reagent and, before the paper is quite dry, add a drop of the test solution. A violet spot, surrounded by a less coloured zone, appears on the yellow paper.

Sensitivity: 0·2 μg. Sn. Concentration limit: 1 in 250,000.

Since ferrous salts have no influence on the test, it may be applied with tin solution which has been reduced by iron wire.

The **reagent** consists of a saturated aqueous solution of cacotheline.

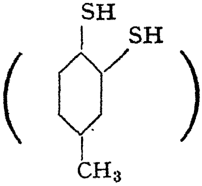
†*9.* **Diazine Green Reagent** (dyestuff formed by coupling diazotised safranine with dimethyl-aniline).—Stannous chloride reduces the blue diazine green to the red safranine, hence the colour change is blue→violet→red. Titanous chloride reacts similarly, but ferrous salts and similar reducing agents have no effect. The reagent is therefore useful in testing for tin in the mixed sulphides of antimony and tin obtained in routine qualitative analysis. The solution of the sulphides in hydrochloric acid is reduced with iron wire and a drop of the reduced solution employed for the test.

Mix 1 drop of the test solution on a spot plate with 1 c.c. of the reagent. The colour changes from blue to violet or red. It is advisable to carry out a blank test.

Sensitivity: 2 μg. Sn. Concentration limit: 1 in 25,000.

The **reagent** consists of a 0·01 per cent aqueous solution of diazine green.

†*10.* **4-Methyl-1 : 2-dimercapto-benzene (or " Dithiol ") Reagent**



red precipitate when warmed with stannous salts in acid solution. The following interfere : silver, lead, mercury, cadmium, arsenic and antimony (yellow precipitates) ; copper, nickel and cobalt (black precipitates) ; bismuth (red precipitate) ; colloidal organic substances (starch, etc.) ; phosphates and nitrites. The hydrochloric acid concentration of the solution should not exceed 15 per cent.

Place 2 drops of the test-solution in a micro-crucible and add 3 drops of the reagent. Warm (not above 60°C) : a red colour or precipitate develops.

Concentration limit : 1 in 500,000.

The **reagent** is prepared by dissolving 0·2 g. of 4-methyl-1 : 2-dimercapto-benzene in 100 c.c. of 1 per cent sodium hydroxide solution and adding 0·3—0·5 g. of thioglycollic acid. The use of the latter in the reagent is not imperative, but it serves to facilitate the reduction of any stannic salt present.

III, 17, REACTIONS OF STANNIC COMPOUNDS

Use a solution of stannic chloride, $SnCl_4,5H_2O$, in dilute hydrochloric acid (this probably contains hexachlorostannic acid :

$$SnCl_4 + 2HCl \rightleftharpoons H_2[SnCl_6] \rightleftharpoons 2H^+ + [SnCl_6]^{--}$$
$$\rightleftharpoons 2H^+ + Sn^{++++} + 6Cl^-)$$

or of ammonium stannichloride, $(NH_4)_2[SnCl_6]$.

1. **Hydrogen Sulphide** : yellow precipitate of stannic sulphide SnS_2 from dilute acid solutions, soluble in colourless or yellow ammonium sulphide solution (forming ammonium sulphostannate) and in concentrated hydrochloric acid, but is insoluble in ammonium carbonate solution (distinction from arsenious sulphide). Yellow stannic sulphide is precipitated upon acidifying the solution of ammonium sulphostannate.

$$SnCl_4 + 2H_2S \rightleftharpoons SnS_2 + 4HCl,$$

or

$$H_2[SnCl_6] + 2H_2S \rightleftharpoons SnS_2 + 6HCl.$$

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + SnS_2.$$

No precipitation of stannic sulphide in the presence of oxalic acid, due to the formation of the stable complex ion of the type $[Sn(C_2O_4)_4(H_2O)_2]^{----}$; this forms the basis of a method of separation of antimony and tin.

2. **Sodium Hydroxide Solution**: gelatinous white precipitate of stannic hydroxide $Sn(OH)_4$, soluble in excess of the precipitant forming sodium stannate $Na_2[SnO_3]$.

$$SnCl_4 + 4NaOH = Sn(OH)_4 + 4NaCl;$$

$$Sn(OH)_4 + 2NaOH = 3H_2O + Na_2[SnO_3].$$

With ammonium hydroxide and sodium carbonate solutions, a similar precipitate is obtained which, however, is insoluble in excess of the reagent.

3. **Mercuric Chloride Solution**: no precipitate (difference from stannous compounds).

4. **Metallic Iron**: reduces stannic salts in hydrochloric acid solution to the stannous condition; filter and test the filtrate with mercuric chloride solution (ferrous salts do not reduce the latter). Similar results are obtained on boiling the solution with copper or antimony.

$$SnCl_4 + Fe = SnCl_2 + FeCl_2.$$

$$H_2[SnCl_6] + Fe = SnCl_2 + FeCl_2 + 2HCl.$$

5. **Cupferron Reagent**: yellowish-white precipitate in the presence of hydrochloric acid.

Dry Tests

(i) *Blowpipe Test.*—All tin compounds when heated with sodium carbonate, preferably in the presence of potassium cyanide, on charcoal give white, malleable and metallic globules of tin which do not mark paper. Part of the metal is oxidised to stannic oxide, especially on strong heating, which forms a white incrustation upon the charcoal.

(ii) *Borax Bead Test.*—A borax bead which has been coloured pale blue by a trace of copper salt becomes a clear ruby red in the reducing flame if a minute quantity of tin is added.

DETECTION AND SEPARATION OF THE METALS IN THE ARSENIC GROUP (GROUP IIB).

The foregoing reactions of the metals of this group provide the facts upon which the following simple table of separation is based. Alternative and more comprehensive schemes are given in Section **V, 12.** The student should prepare, or obtain from the teacher, a solid mixture soluble in hydrochloric acid, or a solution containing these elements, and work through the table in order to familiarise himself with it.

The sulphides are precipitated in the presence of hydrochloric acid and then separated from those of Group IIA by warming for a few minutes with yellow ammonium sulphide solution, the filtrate being employed for the tests. If no metals of Group IIA are present, the ammonium sulphide treatment is, of course, unnecessary.

III, 18. Table XIX.—Analysis of the Arsenic Group (Group IIB).

The filtrate from the copper group may contain the thio salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. Dilute with a little water, add dilute HCl in slight excess (*i.e.*, until acid to litmus), warm, filter and wash. Reject the filtrate. The residue upon the filter may contain As_2S_5, Sb_2S_5, Sb_2S_3, SnS_2 and S.* Boil the precipitate gently with 10 c.c. of concentrated HCl for 5 minutes, dilute with a little water and filter.

Residue. May contain As_2S_3.	**Filtrate.** May contain $SbCl_3$ (or $H[SbCl_4]$) and $SnCl_4$ (or $H_2[SnCl_6]$).
Either—Heat gently for 2–3 minutes with water and powdered ammonium carbonate until dissolved (filter, if necessary), acidify with dilute HCl. Yellow ppt. of As_2S_3. **As present.** *Or*—Dissolve ppt. in concentrated HNO_3, or in concentrated HCl and a little solid $KClO_3$, evaporate off most of the acid, add excess of NH_4OH solution and then magnesia mixture and shake: white crystalline ppt. of $Mg(NH_4)AsO_4$. Dissolve ppt. in dilute HCl (1 : 1) and pass H_2S. Yellow ppt. of As_2S_3. **As present.**	Divide into two parts : *First portion.*—Make just alkaline with NH_4OH, add 4–5 grams of oxalic acid, boil and pass H_2S. Orange ppt. of Sb_2S_3. **Sb present.** *Second portion.*—Partially neutralise the liquid, add 6–12 inches of clean iron wire, heat for 5 minutes to reduce the $SnCl_4$ to $SnCl_2$, and filter into a solution of $HgCl_2$. White ppt. of Hg_2Cl_2 or grey ppt. of Hg. **Sn present.**

THE IRON AND ZINC GROUP (GROUP III)

IRON, ALUMINIUM, CHROMIUM, NICKEL, COBALT, MANGANESE AND ZINC

The metals of this group are not precipitated by the group reagents for Groups I and II, but are all precipitated, in the presence of ammonium chloride, by ammonium sulphide from their solutions made alkaline with ammonium hydroxide solution. The metals, with the exception of aluminium and chromium which are precipitated as the hydroxides owing to the complete hydrolysis of the sulphides in aqueous solution, are precipitated as the sulphides. Iron, aluminium and chromium are precipitated as the hydroxides by ammonium hydroxide solution in the presence of ammonium chloride, whilst the other metals of the group remain in solution and may be precipitated as sulphides by ammonium sulphide. It is therefore usual to subdivide the group into the iron group (iron, aluminium and chromium) or Group IIIA and the zinc group (nickel, cobalt, manganese and zinc) or Group IIIB.

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* If Group IIA absent, commence here.

THE IRON GROUP (GROUP IIIA)

IRON, Fe

Pure iron is a silver-white, tenacious and ductile metal. The commercial metal is rarely pure and usually contains small quantities of the carbide, silicide, phosphide and sulphide of iron, and a little graphite. Iron dissolves in dilute and concentrated hydrochloric acid and in dilute sulphuric acid with the evolution of hydrogen and the formation of ferrous salts ; with hot concentrated sulphuric acid, sulphur dioxide and ferric sulphate are produced. Ferrous and ammonium nitrates are obtained with cold dilute nitric acid, whilst a more concentrated acid yields a ferric salt and either nitrous oxide or nitric oxide depending upon the experimental conditions. Cold concentrated nitric acid renders iron *passive* ; in this state it does not react with dilute nitric acid nor does it displace copper from an aqueous solution of a copper salt.

$$Fe + 2HCl = FeCl_2 + H_2 ;$$

$$Fe + H_2SO_4 \text{ (dilute)} = FeSO_4 + H_2 ;$$

$$2Fe + 6H_2SO_4 \text{ (conc.)} = Fe_2(SO_4)_3 + 6H_2O + 3SO_2 ;$$

$$4Fe + 10HNO_3 \text{ (cold, dilute)} = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O ;$$

$$Fe + 4HNO_3 \text{ (conc.)} = Fe(NO_3)_3 + NO + 2H_2O ;$$

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + N_2O + 5H_2O.$$

Iron forms two important series of salts : the ferrous salts derived from ferrous oxide FeO in which the metal is divalent, and the ferric salts, derived from ferric oxide Fe_2O_3 and containing trivalent iron.

III, 19. REACTIONS OF THE FERROUS ION, Fe^{++}

Use a freshly prepared solution of ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, acidified with a little dilute sulphuric acid. (Solutions of ferrous salts are pale green.)

1. **Sodium Hydroxide Solution** : white precipitate of ferrous hydroxide $Fe(OH)_2$ in the complete absence of air, insoluble in excess, but soluble in acids. Upon exposure to air, ferrous hydroxide is rapidly oxidised, yielding ultimately reddish-brown ferric hydroxide. Under ordinary conditions it appears as a dirty green precipitate ; the addition of hydrogen peroxide immediately oxidises it to ferric hydroxide.

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4 ;$$
$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3.$$

2. **Ammonium Hydroxide Solution** : precipitation of ferrous hydroxide occurs as in reaction *1*. In the presence of excess of ammonium chloride solution, the common ion effect (Section **I, 14**) of the ammonium ions lowers the concentration of the hydroxyl ions to such an extent that the solubility product of ferrous hydroxide $Fe(OH)_2$ is not attained and precipitation does not occur. Similar remarks apply to the other divalent elements of Group III, nickel, cobalt, zinc and manganese and also to magnesium.

3. **Hydrogen Sulphide** : no precipitation takes place in acid solution since the sulphide ion concentration, $[S^{--}]$, is insufficient to exceed the solubility product of ferrous sulphide (see Sections **I, 15** and **I, 16**). If the hydrogen ion concentration is reduced, and the sulphide ion concentration correspondingly increased, by the addition of sodium acetate solution, partial precipitation of black ferrous sulphide FeS occurs. Precipitation is almost complete in alkaline solution (*vide infra*).

4. **Ammonium Sulphide Solution** : black precipitate of ferrous sulphide FeS, readily soluble in acids with evolution of hydrogen sulphide. The moist precipitate becomes brown upon exposure to air, due to its oxidation to basic ferric sulphate $Fe_2O(SO_4)_2$.

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4 ;$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

5. **Potassium Cyanide Solution*** : yellowish-brown precipitate of ferrous cyanide $Fe(CN)_2$, soluble in excess of the precipitant forming a yellow solution of potassium ferrocyanide $K_4[Fe(CN)_6]$.

$$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4 ;$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6].$$

Potassium ferrocyanide is a complex salt, and does not give the typical ferrous ion reactions with ammonium sulphide or sodium hydroxide solutions (compare Section **I, 20**) ; the iron present may be detected by first decomposing the compound by boiling with concentrated sulphuric acid (*caution*: poisonous carbon monoxide is evolved).

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* *Very poisonous* ; in acid solution the volatile and highly poisonous hydrogen cyanide HCN is produced.

$$K_4[Fe(CN)_6] + 6H_2O + 6H_2SO_4 = FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO.$$

6. **Potassium Ferrocyanide Solution**: in the complete absence of air, a white precipitate of ferrous ferrocyanide $Fe_2[Fe(CN)_6]$, or of potassium ferrous ferrocyanide $K_2Fe[Fe(CN)_6]$, is produced, the compound formed depending upon the relative amounts of the ferrous salt and the reagent. Under ordinary atmospheric conditions a pale blue precipitate is obtained; partial oxidation to ferric ferrocyanide or Prussian blue occurs.

$$FeSO_4 + K_4[Fe(CN)_6] = K_2Fe[Fe(CN)_6] + K_2SO_4;$$

$$2FeSO_4 + K_4[Fe(CN)_6] = Fe_2[Fe(CN)_6] + 2K_2SO_4;$$

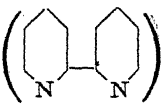
$$4K_2Fe[Fe(CN)_6] + O_2 + 2H_2SO_4 = Fe_4[Fe(CN)_6]_3 + K_4[Fe(CN)_6] + 2K_2SO_4 + 2H_2O.$$

7. **Potassium Ferricyanide Solution**: dark blue precipitate of ferrous ferricyanide or Turnbull's blue $Fe_3[Fe(CN)_6]_2$ from dilute solutions of ferrous salts. It is decomposed by sodium or potassium hydroxide solution, yielding ferrous hydroxide and alkali ferricyanide.

$$3FeSO_4 + 2K_3[Fe(CN)_6] = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4;$$

$$Fe_3[Fe(CN)_6]_2 + 6KOH = 2K_3[Fe(CN)_6] + 3Fe(OH)_2.$$

8. **Ammonium Thiocyanate Solution**: no colouration is obtained with pure ferrous salts (distinction from ferric salts).

†*9.* **αα'-Dipyridyl Reagent**  deep red complex bivalent cation with ferrous salts in mineral acid solution. Ferric iron does not react. Other metallic ions react with the reagent in acid solution, but the intensities of the resultant colours are so feeble that they do not interfere with the test for iron provided an excess of the reagent is employed. Large amounts of halides and sulphates reduce the solubility of the ferrous-dipyridyl complex and a red precipitate may be formed.

Treat a drop of the acidified test solution with 1 drop of the reagent on a spot plate: a red colouration is obtained. Alternatively, treat drop-reaction paper (Whatman No. 3 MM., 1st quality) which has been impregnated with the reagent and dried, with a drop of the test solution: a red or pink spot is produced.

Sensitivity: 0·03 μg. Fe^{++}. Concentration limit: 1 in 1,666,000

If appreciable quantities of ferric salts are present, it is best to carry out the reaction in a micro-crucible lined with paraffin wax and to fix the ferric iron as $[FeF_6]^{---}$ by the addition of a few drops of potassium fluoride solution.

The **reagent** is prepared by dissolving 0·01 g. of $\alpha\alpha'$-dipyridyl in 0·5 c.c. of alcohol or in 0·5 c.c. of 0·1*N*-hydrochloric acid.

†*10*. **Dimethylglyoxime Reagent**: soluble red ferrous dimethylglyoxime in ammoniacal solution. Ferric salts give no colouration, but nickel, cobalt and large quantities of copper salts interfere and must be absent. The test may be carried out in the presence of potassium cyanide solution in which nickel dimethylglyoxime (compare Section **III, 25**) dissolves.

Mix a drop of the test solution with a small crystal of tartaric acid; introduce a drop of the reagent, followed by 2 drops of ammonia solution. A red colouration appears.

Sensitivity: 0·04 μg. Fe^{++}. Concentration limit: 1 in 125,000.

The colouration fades on standing owing to the oxidation of the ferrous complex.

The **reagent** consists of a 1 per cent alcoholic solution of dimethylglyoxime.

III, 20. REACTIONS OF THE FERRIC ION, Fe^{+++}

Use a solution of ferric chloride, $FeCl_3,6H_2O$. (All ferric solutions are yellowish-red; this is the colour of the ferric ion.)

1. **Ammonium Hydroxide Solution**: reddish-brown, gelatinous precipitate of ferric hydroxide $Fe(OH)_3$, insoluble in excess of the reagent, but soluble in acids.

The solubility product of ferric hydroxide is so small ($1{\cdot}1 \times 10^{-36}$) that complete precipitation takes place even in the presence of ammonium salts (distinction from ferrous iron, nickel, cobalt, manganese, zinc and magnesium). Precipitation does not occur in the presence of certain organic acids (see reaction *9* below). Ferric hydroxide is converted on strong heating into ferric oxide; the ignited oxide is difficulty soluble in dilute acids, but dissolves on vigorous boiling with concentrated hydrochloric acid.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl;$$

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

2. **Sodium Hydroxide Solution**: reddish-brown precipitate of ferric hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium).

3. **Hydrogen Sulphide**: reduced to ferrous salt in the presence of acid, with separation of sulphur.

$$2FeCl_3 + H_2S = FeCl_2 + 2HCl + S.$$

4. **Ammonium Sulphide Solution** : black precipitate, consisting of ferrous sulphide and sulphur, from acid solutions. From alkaline solutions, a black precipitate of ferric sulphide Fe_2S_3 is formed ;* this is readily soluble in dilute hydrochloric acid forming ferrous chloride and sulphur.

$$2FeCl_3 + 3(NH_4)_2S = Fe_2S_3 + 6NH_4Cl ;$$
$$Fe_2S_3 + 4HCl = 2FeCl_2 + S + 2H_2S.$$

5. **Potassium Ferrocyanide Solution** : intense blue precipitate of ferric ferrocyanide (Prussian blue) $Fe_4[Fe\ CN)_6]_3$ in neutral or faintly acid solutions. The precipitate is insoluble in dilute hydrochloric acid, but dissolves in oxalic acid solution, in concentrated hydrochloric acid and also in a large excess of the precipitant with the formation of a blue solution. It is decomposed by solutions of caustic alkalis.

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl;$$
$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4[Fe(CN)_6] + 4Fe(OH)_3.$$

6. **Potassium Ferricyanide Solution** : a brown colouration is produced, due to ferric ferricyanide $Fe[Fe(CN)_6]$, or, alternatively, to non-ionised ferric cyanide (distinction from ferrous salts).

$$FeCl_3 + K_3[Fe(CN)_6] = Fe[Fe(CN)_6] + 3KCl.$$
$$FeCl_3 + K_3[Fe(CN)_6] \rightleftharpoons 2Fe(CN)_3 + 3KCl.$$

7. **Sodium Phosphate Solution** : yellowish-white precipitate of ferric phosphate $FePO_4$, readily soluble in mineral acids, but insoluble in acetic acid.

$$FeCl_3 + Na_2HPO_4 = FePO_4 + HCl + 2NaCl \qquad (i) ;$$
$$HCl + Na_2HPO_4 = NaH_2PO_4 + NaCl \qquad (ii) ;$$
$$\overline{FeCl_3 + 2Na_2HPO_4 = FePO_4 + 3NaCl + NaH_2PO_4} \qquad (iii).$$

It is evident from the equations that for the complete precipitation of iron as phosphate it is necessary to use excess of the reagent to react with the liberated hydrogen chloride. This is avoided by the addition of excess of sodium acetate solution, since acetic acid is produced { equation (iv) } in which ferric phosphate is insoluble, and precipitation is quantitative.

$$Na.C_2H_3O_2 + HCl = H.C_2H_3O_2 + NaCl \qquad (iv).$$

The net result is :

$$FeCl_3 + Na_2HPO_4 + Na.C_2H_3O_2 = FePO_4 + H.C_2H_3O_2 + 3NaCl.$$

8. **Sodium Acetate Solution** : reddish-brown colouration, attributed variously to ferric acetate $Fe(C_2H_3O_2)_3$ or to the complex salt $[Fe_3(OH)_2(C_2H_3O_2)_6]C_2H_3O_2$ or to colloidal ferric hydroxide; upon largely diluting and boiling the solution, the iron is precipitated as basic ferric acetate $Fe(OH)_2.C_2H_3O_2$.

$$FeCl_3 + 3Na.C_2H_3O_2 = 3NaCl + Fe(C_2H_3O_2)_3;$$

$$Fe(C_2H_3O_2)_3 + 2H_2O = Fe(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

$$3FeCl_3 + 2H_2O + 9Na.C_2H_3O_2 = [Fe_3(OH)_2(C_2H_3O_2)_6]C_2H_3O_2 + 9NaCl + 2H.C_2H_3O_2;$$

$$[Fe_3(OH)_2(C_2H_3O_2)_6]C_2H_3O_2 + 4H_2O = 3Fe(OH)_2.C_2H_3O_2 + 4H.C_2H_3O_2.$$

Reactions *7* and *8* are combined for the removal of the phosphate radical from solutions in which it interferes with the normal course of analysis (see Sects. **V, 5** and **VI, 2**); they are also affected by the presence of organic acids (tartaric, citric and malic acids) and by polyatomic alcohols (*e.g.*, glycerol, mannitol, various sugars), and special procedures must be adopted in the ordinary course of analysis when these are present (see Chapter VI).

9. **Cupferron Reagent** (the ammonium salt of nitroso-phenyl-hydroxyl-amine, $C_6H_5N(NO)ONH_4$): reddish-brown precipitate in the presence of hydrochloric acid. No precipitate is given by the salts of aluminium and chromium under these conditions, *i.e.*, in strongly acid solution. The precipitate is soluble in ether, is insoluble in acids, and on treatment with ammonium hydroxide solution is converted into ferric hydroxide.

$$FeCl_3 + 3C_6H_5N(NO)ONH_4 = 3NH_4Cl + [C_6H_5N(NO)O]_3Fe.$$

The *reagent* is prepared by dissolving 2 grams of the solid in 100 c.c. of distilled water, but does not keep well. It is recommended that a piece of ammonium carbonate be placed in the stock bottle; this enhances the stability.

10. **Ammonium Thiocyanate Solution**: deep red colouration (difference from ferrous salts). The colouration was formerly attributed to undissociated ferric thiocyanate, but is now known to be due to the ferri-thiocyanate ion, $[Fe(CNS)_6]^{---}$. The reaction is a reversible one and hence the sensitivity is increased by the addition of excess of the reagent. The ferric ferri-thiocyanate is more soluble in ether and in amyl alcohol than in water; accordingly upon shaking with either of these solvents the red colour passes into the organic layer (compare Section **I, 42**). Phosphates, arsenates, borates, iodates, sulphates, acetates, oxalates, tartrates, citrates and the corresponding free acids interfere with the test. Fluorides and mercuric chloride bleach the colour because of the formation of $[FeF_6]^{---}$ and $[Hg(CNS)_4]^{--}$ ions respectively. The presence of nitrites should be avoided, for in acid solution they form nitrosyl thiocyanate NO.CNS which yields a red colour, disappearing on heating, similar to that with ferric iron.

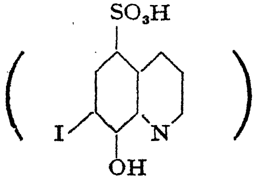
$$2FeCl_3 + 6NH_4CNS \rightleftharpoons Fe[Fe(CNS)_6] + 6NH_4Cl.$$

†The reaction is well adapted as a spot test and may be carried out as follows. Place a drop of the test solution on a spot plate and add 1 drop of 1 per cent ammonium thiocyanate solution. A deep red colouration appears.

Sensitivity: 0·25 μg. Fe^{+++}. Concentration limit: 1 in 200,000.

Coloured salts, *e.g.*, those of copper, chromium, cobalt and nickel, reduce the sensitivity of the test.

†*11.* **7-Iodo-8-hydroxyquinoline-5-sulphonic Acid (or Ferron) Reagent**



green or greenish-blue colouration with ferric salts in faintly acid solution (*p*H 2·5–3·0). Ferrous iron does not react: only copper interferes.

Place a few drops of the slightly acid test solution in a micro test-tube and add 1 drop of the reagent. A green colouration appears.

Sensitivity: 0·5 μg. (in 5 ml.). Concentration limit: 1 in 10,000,000.

The **reagent** consists of a 0·2 per cent aqueous solution of 7-iodo-8-hydroxyquinoline-5-sulphonic acid.

Reduction of ferric to ferrous compounds.—This may be accomplished by nascent hydrogen (*e.g.*, from zinc and dilute hydrochloric or sulphuric acid), hydrogen sulphide, sulphur dioxide, stannous chloride, hydriodic acid or hydrazine sulphate.

$$FeCl_3 + H = FeCl_2 + HCl;$$
$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl;$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4;$$
$$2FeCl_3 + 2HI = 2FeCl_2 + I_2 + 2HCl.$$

Oxidation of ferrous to ferric compounds.—Oxidation occurs slowly upon exposure to air. Rapid oxidation is effected by concentrated nitric acid, hydrogen peroxide, concentrated hydrochloric acid and potassium chlorate, aqua regia, potassium permanganate, potassium dichromate and ceric sulphate in acid solution.

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + 2H_2O + NO;$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O;$$

$$K_2Cr_2O_7 + 6FeSO_4 + 8H_2SO_4 = 3Fe_2(SO_4)_3 + 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Distinctive tests for ferrous and ferric salts.—These are summarised in the following table. The solution should be slightly acid with hydrochloric acid.

Reagent	*Ferrous salt*	*Ferric salt*
Potassium ferrocyanide solution.	White or pale-blue precipitate.	Deep-blue precipitate (Prussian blue).
Potassium ferricyanide solution.	Deep-blue precipitate (Turnbull's blue).	No precipitate; brown colouration.
Ammonium thiocyanate solution.	No colouration in complete absence of ferric salts.	Deep-red colouration, discharged by mercuric chloride solution.
Ammonium hydroxide solution	White to greenish-white precipitate.	Reddish-brown precipitate.

Dry Tests

(i) *Blowpipe test.*—When iron compounds are heated on charcoal with sodium carbonate, grey metallic particles of iron are produced; these are ordinarily difficult to see, but can be separated from the charcoal by means of a magnet.

(ii) *Borax bead test.*—With a small quantity of iron, the bead is yellowish-brown while hot and yellow when cold in the oxidising flame*, and pale green in the reducing flame.

ALUMINIUM, Al

Aluminium is a white, ductile and malleable metal; the powder is grey. The metal is little affected by cold dilute sulphuric acid, but dissolves readily in the hot concentrated acid with the evolution of sulphur dioxide. Nitric acid renders the metal passive; this may be due to the formation of a protective film of oxide. It is readily soluble in hydrochloric acid (dilute and concentrated) with the evolution of hydrogen. With caustic alkalis a solution of an aluminate is formed.,

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* With large quantities of iron, the bead is reddish-brown in the oxidising flame.

$$2Al + 4H_2SO_4 = Al_2(SO_4)_3 + SO_2 + 2H_2O\ ;$$

$$2Al + 6HCl = 2AlCl_3 + 3H_2\ ;$$

$$2Al + 2NaOH + 2H_2O = 2Na[AlO_2] + 3H_2.$$

Aluminium forms only one series of salts derived from the oxide Al_2O_3.

III, 21. REACTIONS OF THE ALUMINIUM ION, Al^{+++}

Use a solution of aluminium sulphate, $Al_2(SO_4)_3,18H_2O$, or of potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$.

1. **Ammonium Hydroxide Solution** : white gelatinous precipitate of aluminium hydroxide $Al(OH)_3$, slightly soluble in excess of the reagent. The solubility is decreased in the presence of ammonium salts owing to the common ion effect (Section **I, 14**). A small proportion of the precipitate passes into solution as colloidal aluminium hydroxide (aluminium hydroxide *sol*) : the *sol* is coagulated on boiling the solution or upon the addition of soluble salts (*e.g.*, ammonium chloride) yielding a precipitate of aluminium hydroxide, known as aluminium hydroxide *gel*. To ensure complete precipitation with ammonium hydroxide solution, the aluminium solution should contain excess of ammonium chloride, the ammonia solution added in slight excess and the mixture boiled until the liquid has a slight odour of ammonia. When freshly precipitated, it dissolves readily in strong acids and bases, but after boiling it becomes difficultly soluble.

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

2. **Sodium Hydroxide Solution** : white precipitate of aluminium hydroxide $Al(OH)_3$, soluble in excess of the reagent with the formation of sodium aluminate $Na[AlO_2]$.

$$Al(OH)_3 + NaOH \rightleftharpoons Na[AlO_2] + 2H_2O.$$

The reaction is a reversible one (compare Section **I, 16**), and any reagent which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration is reduced owing to the formation of the slightly dissociated and unstable ammonium hydroxide, which can be readily removed as ammonia gas on heating) or by the addition of acid; in the latter case a large excess of acid causes the precipitated hydroxide to re-dissolve.

$$Na[AlO_2] + NH_4Cl + H_2O = Al(OH)_3 + NH_3 + NaCl;$$
$$Na[AlO_2] + HCl + H_2O = Al(OH)_3 + NaCl;$$
$$Al(OH)_3 + 3HCl \rightleftharpoons AlCl_3 + 3H_2O.$$

The precipitation of aluminium hydroxide by solutions of sodium and ammonium hydroxide does not take place in the presence of tartaric acid, citric acid, malic acid, sugars and other organic hydroxy compounds, due to the formation of soluble complex salts. These organic substances must therefore be decomposed by gentle ignition or by evaporating with concentrated sulphuric or nitric acid before aluminium can be precipitated in the ordinary course of qualitative analysis.

3. **Ammonium Sulphide Solution**: white precipitate of aluminium hydroxide. The sulphide of aluminium is completely hydrolysed in the presence of water (compare Section **I, 40**); it exists only in the dry condition.

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3H_2S + 6NH_4Cl.$$
$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

4. **Sodium Acetate Solution**: no precipitate is obtained in cold neutral solutions, but on boiling with excess of the reagent, a voluminous precipitate of basic aluminium acetate $Al(OH)_2.C_2H_3O_2$ is formed.

$$Al_2(SO_4)_3 + 6Na.C_2H_3O_2 = 2Al(C_2H_3O_2)_3 + 3Na_2SO_4;$$
$$Al(C_2H_3O_2)_3 + 2H_2O \rightleftharpoons Al(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

5. **Sodium Phosphate Solution**: white gelatinous precipitate of aluminium phosphate $AlPO_4$, insoluble in acetic acid, but soluble in mineral acids and in solutions of caustic alkalis.

$$Al_2(SO_4)_3 + 2Na_2HPO_4 = 2AlPO_4 + 2Na_2SO_4 + H_2SO_4;$$
$$H_2SO_4 + 2Na_2HPO_4 = 2NaH_2PO_4 + Na_2SO_4;$$

$$Al_2(SO_4)_3 + 4Na_2HPO_4 = 2AlPO_4 + 3Na_2SO_4 + 2NaH_2PO_4.$$
$$AlPO_4 + 4NaOH = Na[AlO_2] + Na_3PO_4 + 2H_2O.$$

6. **Sodium Carbonate Solution**: white precipitate of aluminium hydroxide, soluble in excess of the precipitant. This is usually attributed to the complete hydrolysis of the initially formed aluminium carbonate, but may be also explained as due to the hydroxyl ions produced by the hydrolysis of the alkali carbonate.

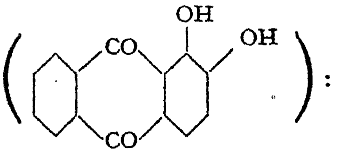
$$Al_2(SO_4)_3 + 3Na_2CO_3 = Al_2(CO_3)_3 + 3Na_2SO_4;$$
$$Al_2(CO_3)_3 + 6H_2O = 2Al(OH)_3 + 3H_2CO_3.$$
$$2Al(OH)_3 + Na_2CO_3 = 2Na[AlO_2] + CO_2 + 3H_2O.$$

7. **"Aluminon" Reagent** (a solution of the ammonium salt of aurine tricarboxylic acid, $C_{22}H_{14}O_9$*): this dyestuff is strongly adsorbed by aluminium hydroxide giving a bright red adsorption complex or "lake." The test is applied to the precipitate of aluminium hydroxide obtained in the usual course of analysis, since certain other elements interfere. Dissolve the aluminium hydroxide precipitate in 5 c.c. of *M* hydrochloric acid, add 5 c.c. of 3*M* ammonium acetate solution and 5 c.c. of 0·1% aqueous solution of the reagent. Shake, allow to stand for 5 minutes, and add excess of ammoniacal ammonium carbonate solution. A bright red precipitate (or colouration), persisting in the alkaline solution, is obtained.

Iron interferes with the test and should be absent. Chromium forms a similar lake in acetate solution, but this is rapidly decomposed by the addition of the ammoniacal ammonium carbonate solution. Beryllium gives a lake similar to that formed by aluminium. Phosphates, when present in *considerable* quantity, prevent the formation of the lake. It is then best to precipitate the aluminium phosphate by the addition of ammonium hydroxide solution; the resultant precipitate is redissolved in dilute acid, and the test applied in the usual way.

The *reagent* is prepared by dissolving 0·25 grams of "aluminon" in 250 c.c. of water.

8. **Alizarin Reagent**



red lake with aluminium hydroxide.

Soak some quantitative filter (or drop-reaction) paper in a saturated

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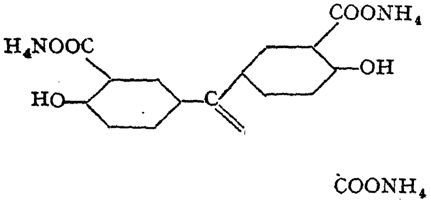
* The constitutional formula of "aluminon" is:

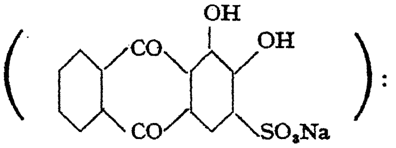


alcoholic solution of alizarin and dry it. Place a drop of the acid test solution on the paper and hold it over ammonia fumes until a violet colour (due to ammonium alizarinate) appears. Dry the paper at 100°C: the violet colour is discharged and a red spot remains.

Sensitivity: 0·15 μg. Al. Concentration limit: 1 in 333,000.

Iron, chromium, uranium, thorium, titanium and manganese interfere, but this may be obviated by using paper previously treated with potassium ferrocyanide. The ions are thus "fixed" on the paper as insoluble ferrocyanides, and the aluminium solution diffuses beyond as a damp ring. Upon adding a drop of a saturated alcoholic solution of alizarin, exposing to ammonia vapour and drying, a red ring of the alizarin-aluminium lake forms round the precipitate. Uranium ferrocyanide, owing to its slimy nature, has a tendency to spread outwards from the spot and thus obscure the aluminium lake; this difficulty is surmounted by dipping the paper after the alizarin treatment in ammonium carbonate solution which dissolves the uranium ferrocyanide.

†9. **Alizarin-S (or Sodium Alizarin Sulphonate) Reagent**



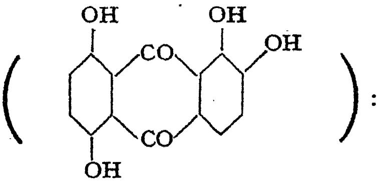
red precipitate or lake in ammoniacal solution, which is fairly stable to dilute acetic acid.

Place a drop of the test solution (which has been treated with just sufficient of *N*-sodium hydroxide solution to give the aluminate ion [AlO]$_2^-$) on a spot plate, add 1 drop of the reagent, then drops of acetic acid until the violet colour just disappears and 1 drop in excess. A red precipitate or colouration appears.

Sensitivity: 0·7 μg. Al. Concentration limit: 1 in 80,000.

A blank test should be made on the sodium hydroxide solution.

†*10*. **Quinalizarin (or 1 : 2 : 5 : 8-Tetrahydroxy-anthraquinone) Reagent**



red precipitate or colouration under the conditions given below.

Place a drop of the test solution upon the reagent paper; hold it for a short time over a bottle containing concentrated ammonia solution and then over glacial acetic acid until the blue colour (ammonium quinalizarinate) first formed disappears and the unmoistened paper regains the brown colour of free quinalizarin. A red-violet or red spot is formed.

Sensitivity: 0·005 μg. Al (drop of 0·1 c.c.). Concentration limit: 1 in 2,000,000.

The **reagent paper** is prepared by soaking quantitative filter paper in a solution obtained by dissolving 0·01 g. of quinalizarin in 2 c.c. of pyridine and then diluting with 20 c.c. of acetone.

Dry Tests

(i) *Blowpipe test.*—Aluminium compounds when heated with sodium carbonate upon charcoal in the blowpipe flame give a white infusible solid, which glows when hot. If the residue be moistened with one or two drops of cobalt nitrate solution and again heated, a blue infusible mass (Thenard's blue, or cobalt meta-aluminate) is obtained. It is important not to use an excess of cobalt nitrate solution since this yields black cobalt oxide Co_3O_4 upon ignition, which masks the colour of the Thenard's blue.

$$2Al_2O_3 + 2Co(NO_3)_2 = 2CoAl_2O_4 + 4NO_2 + O_2.$$

An alternative method for carrying out this test is to soak some ashless filter paper in the aluminium salt solution, add a drop or two of cobalt nitrate solution and then to ignite the filter paper in a crucible ; the residue is coloured blue.

CHROMIUM, Cr

Chromium is a white crystalline metal and is not appreciably ductile or malleable. The metal is soluble in hydrochloric acid yielding the blue chromous chloride $CrCl_2$ if air is excluded, otherwise chromic chloride $CrCl_3$ is formed ; hydrogen is evolved. Dilute sulphuric acid reacts similarly forming chromous sulphate $CrSO_4$ in the absence of air, and chromic sulphate $Cr_2(SO_4)_3$ in the presence of air. Concentrated sulphuric acid, dilute and concentrated nitric acid induce passivity.

The normal oxide of chromium is the green sesquioxide Cr_2O_3, from which the chromic salts are derived. Chromous salts, corresponding to the oxide CrO, are extremely readily oxidised in air to chromic salts ; the former are rarely encountered in elementary qualitative analysis and will therefore not be considered here. An acidic oxide, chromium trioxide CrO_3, forming red deliquescent crystals, is known : this gives rise to the coloured chromates (*e.g.*, K_2CrO_4 or K_2O,CrO_3) and dichromates (*e.g.*, $K_2Cr_2O_7$ or $K_2O,2CrO_3$), which are discussed in Section **IV, 33.**

III, 22. REACTIONS OF THE CHROMIC ION, Cr^{+++}

Use a solution of chromic chloride, $CrCl_3,6H_2O$, or of chrome alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. (Chromic salts are either green or violet in solution.)

1. **Ammonium Hydroxide Solution** : grey-green to grey-blue gelatinous precipitate of chromic hydroxide $Cr(OH)_3$, slightly soluble in excess of the precipitant in the cold forming a violet or pink solution containing complex chrome-ammines; upon boiling the solution, chromium hydroxide is precipitated. Hence for complete precipitation of chromium as the hydroxide, it is essential that the solution be boiling and excess of ammonium hydroxide solution be avoided.

$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl.$$
$$Cr(OH)_3 + 6NH_4OH = [Cr(NH_3)_6](OH)_3 + 6H_2O.$$

2. **Sodium Hydroxide Solution**: precipitate of chromic hydroxide, readily soluble in acids and also in excess of the precipitant in the cold forming a green solution containing sodium chromite $Na[CrO_2]$. Upon boiling the latter solution, hydrolysis occurs and the chromium is almost quantitatively re-precipitated as the hydroxide (distinction from aluminium).

$$Cr(OH)_3 + NaOH \rightleftharpoons Na[CrO_2] + 2H_2O.$$

If hydrogen peroxide is added to the sodium chromite solution, a yellow solution of sodium chromate is produced, which may be identified by the perchromic acid reaction (Section **IV, 33,** reaction *4*; reaction *6* below) or by the diphenylcarbazide reagent (Section **IV, 33**), reaction *10*).

$$2Na[CrO_2] + 3H_2O_2 + 2NaOH = 2Na_2[CrO_4] + 4H_2O.$$

3. **Ammonium Sulphide Solution or Sodium Carbonate Solution**: precipitate of chromic hydroxide. The explanation is similar to that given under Aluminium (Section **III, 21,** reactions *3* and *6*). Chromium sulphide is completely hydrolysed in aqueous solution.

4. **Sodium Acetate Solution**: no precipitate even on boiling the solution.

In the presence of considerable amounts of iron and aluminium salts, the precipitate of basic acetates obtained on boiling contains the basic acetate $Cr(OH)_2.C_2H_3O_2$. If the chromium is present in excess, only a fraction of all the metals will be precipitated as basic acetates, whilst some aluminium, iron and chromium will remain in the filtrate. The basic acetate method of separation (see Sect. **VI, 2**) is therefore uncertain in the presence of a large concentration of chromium.

The precipitation of chromic hydroxide is prevented by the presence of certain organic compounds in solution (see under Aluminium, Sect. **III, 21,** reaction *6*).

5. **Sodium Phosphate Solution**: green precipitate of chromium phosphate $CrPO_4$, soluble in mineral acids, but practically insoluble in cold dilute acetic acid.

$$CrCl_3 + 2Na_2HPO_4 = CrPO_4 + 3NaCl + NaH_2PO_4.$$

6. **Sodium Peroxide.**—A yellow solution of a chromate is produced by adding excess of sodium hydroxide solution to a solution of a chromic salt, followed by sodium peroxide in small quantities and then boiling the resultant mixture. The chromate is identified: (*a*) by adding ether* (3 c.c.; *highly inflammable*), acidifying with dilute sulphuric acid and then adding hydrogen peroxide, when it will be found that the ether layer is coloured blue, due to the dissolution of the unstable perchromic acid in it; or (*b*) by acidifying with acetic acid and adding barium chloride and sodium acetate solution when a yellow precipitate of barium chromate is formed.

$$2CrCl_3 + 3Na_2O_2 + 4NaOH = 2Na_2CrO_4 + 6NaCl + 2H_2O.$$

†7. **Test with Diphenylcarbazide Reagent after Conversion into Chromate.**—Chromic chromium may be converted into chromate

(i) by oxidation with bromine water in the presence of alkali (*i.e.*, by hypobromite); the excess of bromine is rendered inactive by the addition of phenol which gives tribromophenol—

$$2Cr^{+++} + 3\ OBr^- + 10\ OH^- = 2CrO_4^{--} + 3Br^- + 5H_2O.$$

(ii) by heating in acid solution with an alkali persulphate in the presence of a trace of a silver salt, which acts as a catalyst in accelerating the oxidation—

$$2Cr^{+++} + 3S_2O_8^{--} + 8H_2O = 2CrO_4^{--} + 16H^+ + 6SO_4^{--}.$$

Large quantities of halides must be absent as they prevent the catalytic action of the silver ions.

Solutions of chromates in dilute mineral acids give a soluble violet compound with the diphenylcarbazide reagent.

Place a drop of the test solution in mineral acid on a spot plate, introduce a drop of saturated bromine water followed by 2–3 drops of 2*N*-potassium hydroxide (the solution must be alkaline to litmus). Mix thoroughly, add a crystal of phenol, then a drop of the diphenylcarbazide reagent, and finally 2*N*-sulphuric acid until the red colour (from the reaction between diphenylcarbazide and alkali) disappears. A blue-violet colouration is obtained.

Sensitivity: 0·25 μg. Cr. Concentration limit: 1 in 2,000,000.

Copper, manganese, nickel and cobalt salts interfere in this procedure because of their precipitation by the alkali.

Alternatively, mix a drop of the acidified test solution on a spot plate with a drop of saturated potassium persulphate solution and a drop of 2 per cent silver nitrate solution, and allow to stand for 2–3 minutes. Add a drop of the diphenylcarbazide reagent. A violet or red colour is formed.

Sensitivity: 0·8 μg. Cr. Concentration limit: 1 in 600,000.

Manganese ions interfere (oxidised to permanganic acid) as do also mercuric salts, molybdates and vanadates, which give blue to violet compounds with the reagent in acid solution. The influence of molybdates can be eliminated by the addition of **saturated oxalic acid** solution thereby forming the complex $H_2[MoO_3(C_2O_4)]$.

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* Alternatively, amyl alcohol or ethyl acetate may be used.

Dry Tests

(i) *Blowpipe test.*—All chromium compounds when heated with sodium carbonate on charcoal yield a green infusible mass of chromium sesquioxide Cr_2O_3.

(ii) *Borax bead test.*—The bead is coloured green in both the oxidising and reducing flames, but is not very characteristic.

(iii) Fusion with sodium carbonate and potassium nitrate in a loop of platinum wire or upon platinum foil or upon the lid of a nickel crucible results in the formation of a yellow mass of alkali chromate.

$$Cr_2(SO_4)_3 + 5Na_2CO_3 + 3KNO_3 = 2Na_2CrO_4 + 3KNO_2 + 3Na_2SO_4 + 5CO_2.$$

DETECTION AND SEPARATION OF THE METALS IN THE IRON GROUP (GROUP IIIA)

In the following table it is assumed that the metals of Groups I and II, if present, have been removed as already described, or that only metals of Group IIIA are present; in the former case, it will be necessary to boil off any hydrogen sulphide present (test fumes with lead acetate paper). As in previous instances, the student should make up for himself, or procure from the teacher, a solution containing some or all of the metals of the group. Phosphates, borates, silicates and organic acids are assumed to be absent. For satisfactory precipitation with the group reagent NH_4OH and NH_4Cl, all of the three metals must be present as *trivalent* cations. It is therefore necessary to test the solution for ferrous iron with potassium ferricyanide solution and, if this is present, it must first be oxidised to the ferric state by boiling the solution with a little concentrated nitric acid.

III, 23. Table XX.—Analysis of the Iron Group (Group IIIA)

Add 2 grams of solid ammonium chloride for each 10 c.c. of solution, heat to boiling, and add dilute NH_4OH solution slowly until the solution just smells of ammonia, boil for 1–2 minutes, filter rapidly and wash.

Residue. May contain $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ and a little $MnO(OH)_2$*. Suspend the ppt. in a little water, add 1–1·5 grams of Na_2O_2 (or excess of NaOH solution, followed by 5 c.c. of H_2O_2), boil until effervescence ceases. Filter and wash.	**Filtrate.** Neglect.

Residue. May contain $Fe(OH)_3$ and $MnO(OH)_2$* Divide into two parts. (1) Dissolve in dilute HCl, and add $K_4[Fe(CN)_6]$ solution. Blue ppt. **Fe present.** (2) Dissolve in nitric acid (1 : 1), add 1 gram of Pb_3O_4, boil gently for 1–2 minutes and allow to settle. Violet solution of $HMnO_4$. **Mn present.**	**Filtrate.** May contain $Na[AlO_2]$ and Na_2CrO_4. If colourless, Cr is absent. If yellow, divide into two parts. (1) Add acetic acid until acid, and then lead acetate solution. Yellow precipitate of $PbCrO_4$. **Cr present.** (2) Acidify with HCl (litmus paper test) and then add NH_4OH until alkaline. Heat to boiling. White gelatinous ppt. of $Al(OH)_3$ (confirm by Thenard's blue test). **Al present.**

THE ZINC GROUP (GROUP IIIB)

Cobalt, Co

Cobalt is a steel-grey, magnetic solid. It dissolves slowly in warm dilute hydrochloric or sulphuric acid, and more rapidly in nitric acid forming cobaltous compounds, which are derived from cobaltous oxide CoO. Two other oxides exist : cobaltic oxide Co_2O_3, giving rise to the extremely unstable cobaltic compounds, and cobaltous cobaltic oxide Co_3O_4. All the oxides of cobalt dissolve in acids yielding cobaltous salts.

$$Co_2O_3 + 6HCl = 2CoCl_2 + Cl_2 + 3H_2O\,;$$
$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4H_2O.$$

Many stable complex compounds containing trivalent cobalt, *e.g.*, potassium cobaltinitrite $K_3[Co(NO_2)_6]$ and potassium cobalticyanide $K_3[Co(CN)_6]$, are known.

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* Small quantities of manganese, if present, are often precipitated at this stage and it is best to test for its presence (see Manganese, Sect. **III, 26**, reaction 2)

III, 24. REACTIONS OF THE COBALTOUS ION, Co

Use a solution of cobalt nitrate, $Co(NO_3)_2,6H_2O$. aqueous solutions of cobaltous salts are pink.)

1. **Sodium Hydroxide Solution** : a blue basic salt is precipitated in the cold ; upon warming with excess of alkali (sometimes merely upon addition of excess of the reagent), the basic salt is converted into pink cobaltous hydroxide $Co(OH)_2$. This hydroxide is transformed into the brownish-black cobaltic hydroxide $Co(OH)_3$ on exposure to the air, or by prolonged boiling of the aqueous suspension ; the change takes place rapidly if an oxidising agent, such as sodium hypochlorite solution or hydrogen peroxide, is added. Cobaltous hydroxide is readily soluble in concentrated solutions of ammonium salts in consequence of the formation of complex salts ; solutions of alkali hydroxides do not, therefore, precipitate cobaltous hydroxide from ammoniacal solution of cobalt salts.

$$Co(NO_3)_2 + NaOH = Co(OH)NO_3 + NaNO_3 ;$$

$$Co(OH)NO_3 + NaOH = Co(OH)_2 + NaNO_3 ;$$

$$2Co(OH)_2 + H_2O + O = 2Co(OH)_3.$$

2. **Ammonium Hydroxide Solution** : precipitate of blue basic salt as in reaction *1*, readily soluble in excess of the precipitant and in solutions of ammonium salts. The brownish-yellow ammoniacal solution turns red on exposure to air, more rapidly upon addition of hydrogen peroxide ; this is due to the formation of complex salts (cobalt-ammines). These are unaffected by alkali hydroxide solution.

$$\begin{aligned}4Co(OH)NO_3 &+ 28NH_4OH + O_2 \\ &= 4[Co(NH_3)_6](OH)_3 + 4NH_4NO_3 + 22H_2O.\end{aligned}$$

The precipitation of cobaltous hydroxide does not take place in the presence of certain organic acids and organic hydroxy compounds, as in the case of aluminium (Section **III, 21**, reaction *2*).

3. **Ammonium Sulphide Solution** : black precipitate of cobalt sulphide CoS from neutral or alkaline solutions, insoluble in excess of the reagent, in acetic acid and in very dilute hydrochloric acid, but is readily soluble in hot concentrated nitric acid and in aqua regia with the separation of sulphur.

$$Co(NO_3)_2 + (NH_4)_2S = CoS + 2NH_4NO_3.$$

$$3CoS + 8HNO_3 = 3Co(NO_3)_2 + 2NO + 3S + 4H_2O.$$

4. **Potassium Cyanide Solution**: reddish-brown precipitate of cobaltous cyanide $Co(CN)_2$, soluble in excess of the reagent to form a brown solution containing potassium cobalt*o*cyanide $K_4[Co(CN)_6]$, analogous to potassium ferrocyanide $K_4[Fe CN)_6]$. When the cobalt*o*cyanide solution is treated *in the cold* with dilute hydrochloric acid, cobaltous cyanide is precipitated.

On prolonged boiling of the brown solution, preferably after the addition of a few drops of hydrogen peroxide or of sodium hypochlorite or of sodium hypobromite solution, it assumes a yellow colour, due to oxidation to potassium cobalt*i*cyanide $K_3[Co(CN)_6]$, analogous to potassium ferricyanide $K_3[Fe(CN)_6]$. The cobalticyanide solution gives no precipitate with acids (distinction from nickel).

$$Co(NO_3)_2 + 2KCN = Co(CN)_2 + 2KNO_3;$$

$$Co(CN)_2 + 4KCN = K_4[Co(CN)_6];$$

$$4K_4[Co(CN)_6] + 2H_2O + O_2 = 4K_3[Co(CN)_6] + 4KOH.$$

$$K_4[Co(CN)_6] + 4HCl = Co(CN)_2 + 4HCN + 4KCl.$$

5. **Potassium Nitrite Solution**: yellow precipitate of potassium cobaltinitrite $K_3[Co(NO_2)_6],3H_2O$ when added in excess to a concentrated solution of a cobalt salt acidified with acetic acid (distinction from nickel). In dilute solution, the precipitate appears only after standing for several hours, or more rapidly on shaking.

$$Co(NO_3)_2 + 2KNO_2 = Co(NO_2)_2 + 2KNO_3;$$

$$Co(NO_2)_2 + 2KNO_2 + 2H.C_2H_3O_2 = Co(NO_2)_3 + K.C_2H_3O_2 + NO + H_2O;$$

$$Co(NO_2)_3 + 3KNO_2 = K_3[Co(NO_2)_6].$$

$$Co(NO_3)_2 + 7KNO_2 + 2H.C_2H_3O_2 = K_3[Co(NO_2)_6] + 2KNO_3 + 2K.C_2H_3O_2 + NO + H_2O.$$

6. **Ammonium Thiocyanate Solution**: a blue solution, due to the cobaltithiocyanate ion $[Co(CNS)_4]^{--}$, is produced by adding concentrated NH_4CNS solution (it is best to add a few crystals of the solid salt to the test solution); if amyl alcohol be added and the solution shaken, the blue colour passes into the alcohol layer (distinction from nickel).

The free acid $H_2[Co(CNS)_4]$ is much more soluble in ether and in amyl alcohol than its salts, hence it is best to strongly acidify the solution with concentrated HCl: the test is thus rendered much more sensitive.

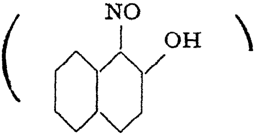
$$Co(NO_3)_2 + 4HCNS = H_2[Co(CNS)_4] + 2HNO_3.$$

The disturbing effect of Fe^{+++} is overcome by the addition of a fluoride solution, thereby forming the highly stable ferri-fluoride ion $[FeF_6]^{---}$; alternatively, a little solid $Na_2S_2O_3$ may be added and the mixture vigorously shaken whereby Fe^{+++} is reduced to Fe^{++} and $Na_2S_4O_6$ is produced.

† The reaction may be employed as a spot test as follows. Upon a spot plate, mix one drop of the test solution with 5 drops of a saturated solution of ammonium thiocyanate in acetone. A green to blue colouration appears.
Sensitivity: 0·5 μg. Co. Concentration limit: 1 in 100,000.

If **iron is present** mix 1–2 drops of the slightly acid test solution with a few milligrams of ammonium or sodium fluoride on a spot plate and then add 5 drops of a 10 per cent solution of ammonium thiocyanate in acetone. A blue colouration is produced.
Sensitivity: 1 μg. Co in the presence of 1000 times the amount of Fe. Concentration limit: 1 in 50,000.

7. α-**Nitroso-β-naphthol Reagent**



reddish-brown precipitate of cobalti-nitroso-β-naphthol $Co(C_{10}H_6O_2N)_3$ in solutions acidified with dilute hydrochloric acid or dilute acetic acid; the precipitate may be extracted by carbon tetrachloride to give a claret-coloured solution. Precipitates are also given by solutions of salts of nickel and ferric iron in Group III. The nickel complex is soluble in dilute hydrochloric acid and the addition of sodium fluoride renders iron innocuous. This is an excellent confirmatory test for cobalt in the Group IIIB precipitate after the speration of the manganese and the zinc.

The **reagent** is prepared by dissolving 1 g. of α-nitroso-β-naphthol in 50 c.c. of glacial acetic acid, followed by dilution with 50 c.c. of water. It does not keep well.

†The details for the use of the reaction as a spot test are as follows. Place a drop of the faintly acid test solution on a piece of drop-reaction paper and add a drop of the above reagent. A brown stain is produced.

Sensitivity: 0·05 μg. Co. Concentration limit: 1 in 1,000,000.

Copper, ferric iron, uranyl and palladous salts interfere. **Copper** is rendered inactive by the addition of 1 drop of 2*N*-hydrochloric acid, 1 drop of 10 per cent potassium iodide solution and a little solid sulphite (to remove liberated iodine): upon introducing a drop of the reagent (1 per cent solution of α-nitroso-β-naphthol in acetone) and 3 drops of saturated sodium acetate solution, a brown colouration appears.

Sensitivity: 0·2 μg. Co in the presence of 2,500 times the amount of copper. Concentration limit: 1 in 250,000.

In the **presence of ferric iron and uranium,** the addition of sodium phosphate precipitates the phosphates of these elements, but only cobalt phosphate reacts immediately with the reagent. Mix one drop of the acidified test solution, 1 drop of the reagent (1 per cent solution of α-nitroso-β-naphthol in acetone) and a few drops of 10 per cent. sodium phosphate solution on a spot plate. A brown colouration appears.

Sensitivity: 0·2–0·8 μg. Co in the presence of 1000 times the amount of U and 200 times the amount of Fe. Concentration limit: 1 in 200,000.

†*8*. **Rubeanic Acid** (**or Dithio-oxamide**) **Reagent** $\{(CS.NH_2)_2\}$: yellowish-brown precipitate. Under similar conditions nickel and copper salts give blue and black precipitates respectively (see under Copper, Section **III, 8**). Large quantities of ammonium salts reduce the sensitivity.

Place a drop of the test solution upon drop-reaction paper, hold it in ammonia vapour, and then add a drop of the reagent. A brown spot or ring is formed.

Sensitivity: 0·03 μg. Co. Concentration limit: 1 in 660,000.

The **reagent** consists of a 1 per cent solution of rubeanic acid in alcohol.

Dry Tests

(i) *Blowpipe test.*—All cobalt compounds when ignited with sodium carbonate on charcoal give grey, slightly metallic beads of cobalt. If these are removed, placed upon filter paper and dissolved by the addition of a few drops of dilute nitric acid, a few drops of concentrated hydrochloric acid added and the filter paper dried, the latter is coloured blue by the cobalt chloride produced.

(ii) *Borax bead test.*—This gives a blue bead in both the oxidising and reducing flames. Cobalt meta-borate $Co(BO_2)_2$, or the complex salt $Na_2[Co(BO_2)_4]$, is formed (see Section **II, 1**). The presence of a large proportion of nickel does not interfere.

NICKEL, Ni

Nickel is a hard, silver-white metal; it is ductile, malleable and very tenacious. Hydrochloric and sulphuric acids, both dilute and concentrated, attack it slowly; dilute nitric acid dissolves it readily, but the concentrated acid induces passivity.

Only one stable series of salts, the nickelous salts, derived from the green nickelous oxide NiO, is known. A brownish-black nickelic oxide Ni_2O_3 exists, but this dissolves in acids forming nickelous compounds.

$$Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2.$$

III, 25. REACTIONS OF THE NICKEL ION, Ni^{++}

Use a solution of nickel sulphate, $NiSO_4,7H_2O$, or of nickel chloride, $NiCl_2,6H_2O$. (Solutions of nickelous salts are green.)

1. **Sodium Hydroxide Solution**: green precipitate of nickelous hydroxide $Ni(OH)_2$, insoluble in excess of the reagent. The precipitate dissolves in ammonium hydroxide solution or in solutions of ammonium salts forming greenish-blue solutions of complex nickelous ammonia ions (see Section **I, 20**) ; these solutions are not oxidised on boiling with free exposure to air, or upon the addition of hydrogen peroxide (difference from cobalt). Nickelous hydroxide is oxidised by sodium hypochlorite solution to black nickelic hydroxide $Ni(OH)_3$.

$$NiSO_4 + 2NaOH = Ni(OH)_2 + Na_2SO_4 ;$$
$$4Ni(OH)_2 + 2H_2O + O_2 = 4Ni(OH)_3.$$

2. **Ammonium Hydroxide Solution**: green precipitate of basic salt, soluble in excess of the reagent forming complex nickel ammonia compounds.

$$NiCl_2 + 2NH_4OH = Ni(OH)Cl + NH_4Cl ;$$
$$Ni(OH)Cl + 7NH_4OH = [Ni(NH_3)_6](OH)_2 + 6H_2O + NH_4Cl.$$

No precipitation takes place with ammonium hydroxide solution in the presence of ammonium salts ; this is because the concentration of hydroxyl ions is so reduced that the solubility product of neither $Ni(OH)Cl$ nor $Ni(OH)_2$ is attained (see Sections **I, 15** and **I, 16**).

3. **Ammonium Sulphide Solution**: black precipitate of nickel sulphide NiS from neutral solutions, slightly soluble in excess of the reagent forming a dark-brown, colloidal solution which runs through the filter paper. If the colloidal solution is boiled or if it is rendered slightly acid with acetic acid and boiled, the colloidal solution (hydrosol) is coagulated and can then be filtered. The presence of large quantities of ammonium chloride prevents the formation of the sol. Nickel sulphide is practically insoluble in cold dilute hydrochloric acid, sp. gr. 1·02 (distinction from the sulphides of manganese and zinc) and in acetic acid, but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur.

$$NiCl_2 + (NH_4)_2S = NiS + 2NH_4Cl.$$
$$3NiS + 8HNO_3 = 3Ni(NO_3)_2 + 2NO + 3S + 4H_2O.$$
$$3NiS + 2HNO_3 + 6HCl = 3NiCl_2 + 2NO + 3S + 4H_2O.$$

4. **Hydrogen Sulphide**: only part of the nickel is slowly precipitated as nickel sulphide from neutral solutions; no precipitation occurs from solutions containing mineral acid or much acetic acid. Complete precipitation occurs, however, from solutions made alkaline with ammonium hydroxide solution, or from solutions containing excess of alkali acetate slightly acid with acetic acid (compare Section **I, 16**).

$$NiCl_2 + H_2S \rightleftharpoons NiS + 2HCl.$$

5. **Potassium Cyanide Solution**: green precipitate of nickelous cyanide $Ni(CN)_2$, readily soluble in excess of the reagent forming the complex salt, potassium nickelocyanide $K_2[Ni(CN)_4]$ (compare Section **I, 20**). If this solution be warmed with sodium hypobromite solution (prepared *in situ* by adding bromine water to sodium hydroxide solution), the complex cyanide is decomposed and a black or brown precipitate is formed (difference from cobalt); the precipitate is variously formulated as $Ni(OH)_3$ or NiO_2. Excess of potassium cyanide solution should be avoided since the bromine water will first react with the excess of cyanide forming cyanogen bromide CNBr; hence it is best to add potassium cyanide solution drop by drop until the initial precipitate is just dissolved.

Careful addition of dilute hydrochloric acid to the solution of potassium nickelocyanide precipitates nickel cyanide.

$$NiCl_2 + 2KCN = Ni(CN)_2 + 2KCl;$$

$$Ni(CN)_2 + 2KCN = K_2[Ni(CN)_4];$$

$$2K_2[Ni(CN)_4] + 9NaOBr + 4NaOH + H_2O$$
$$= 2Ni(OH)_3 + 4KCNO + 4NaCNO + 9NaBr;$$

$$KCN + Br_2 = CNBr + KBr;$$

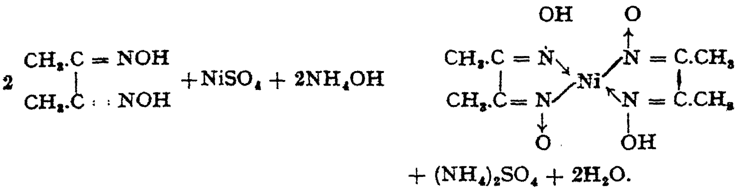
$$K_2[Ni(CN)_4] + 2HCl = Ni(CN)_2 + 2HCN + 2KCl.$$

6. **Potassium Nitrite Solution**: no precipitate is produced in the presence of acetic acid (difference from cobalt).

7. **α-Nitroso-β-naphthol Reagent** $\{C_{10}H_6(NO)OH\}$: brown precipitate of composition $Ni(C_{10}H_6O_2N)_2$, soluble in dilute hydrochloric acid (difference from cobalt, which gives a reddish-brown precipitate, insoluble in dilute hydrochloric acid).

8. **Dimethylglyoxime Reagent*** ($C_4H_8O_2N_2$) red precipitate of nickel dimethylglyoxime in solutions just alkaline with ammonium hydroxide solution or containing sodium acetate; precipitation is accelerated, especially in dilute solution, by boiling.

*This is sometimes known as Tschugaeff's reagent, after its discoverer (1905).



Ferrous iron (compare Section **III, 19**), bismuth and more than about 10 times the quantity of cobalt interfere. The influence of interfering elements, including ferric iron, is eliminated by the addition of a tartrate. When large quantities of cobalt salts are present, these react with the dimethylglyoxime and a special procedure must be adopted (see below). Oxidising agents must be absent.

The *reagent* is prepared by dissolving 1 g. of dimethylglyoxime in 100 c.c. of rectified spirit.

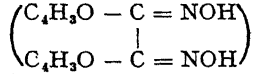
† The spot test technique is as follows. Place a drop of the test solution on drop-reaction paper, add a drop of the above reagent and hold the paper over ammonia vapour. Alternatively, place a drop of the test solution and a drop of the reagent on a spot plate, and add a drop of dilute ammonia solution. A red spot or precipitate (or colouration) is produced.

Sensitivity: 0·16 μg. Ni. Concentration limit: 1 in 300,000.

Detection of traces of nickel in cobalt salts. The solution containing the cobalt and nickel is treated with excess of concentrated potassium cyanide solution, followed by " 10-volume " hydrogen peroxide whereby the complex cyanides $K_3[Co(CN)_6]$ and $K_2[Ni(CN)_4]$ respectively are formed. Upon adding 40 per cent formaldehyde solution the potassium cobalticyanide is unaffected (and hence remains inactive to dimethylglyoxime) whereas the potassium nickelocyanide is decomposed with the formation of nickel cyanide, which reacts immediately with the dimethylglyoxime.

$$K_2[Ni(CN)_4] + 2H.CHO = Ni(CN)_2 + 2CH_2(CN)OK.$$

$$Ni(CN)_2 + 2C_4H_8O_2N_2 = Ni(C_4H_7O_2N_2)_2 + 2HCN.$$



†*9*. **α-Furil-dioxime Reagent** $\left(\begin{array}{c} C_4H_3O - C = NOH \\ | \\ C_4H_3O - C = NOH \end{array}\right)$: red precipitate in slightly ammoniacal solution.

Place a few drops of the slightly ammoniacal test solution in a micro-test-tube and add a few drops of the reagent. A red precipitate or colouration is formed. Alternatively, the reaction may be carried out on a spot plate.

Sensitivity: 0·02 μg. Ni. Concentration limit: 1 in 6,000,000.

The reaction is not disturbed by silver or copper, or by ferric iron, chromium or aluminium in the presence of ammoniacal tartrate solution; if zinc is present, ammonium chloride should first be added; cobaltous ions repress the sensitivity and should be oxidised to the cobaltic state with hydrogen peroxide; ferrous iron interferes and should be oxidised and alkaline tartrate solution added before applying the test.

The **reagent** consists of a 10 per cent solution of α-furil-dioxime in alcohol.

†*10.* **Rubeanic Acid Reagent** $\{(CS.NH_2)_2\}$; blue or violet precipitate or colouration in ammoniacal solution. Copper and cobalt, as well as iron, salts interfere with the reaction and should be absent.

Place a drop of the test solution upon drop-reaction paper, hold it over ammonia vapour, and add a drop of the reagent. A blue or blue-violet spot is obtained.

Sensitivity: 0·01 μg. Ni (in 0·015 c.c.). Concentration limit: 1 in 1,250,000.

The **reagent** consists of a 1 per cent solution of rubeanic acid in alcohol.

Dry Tests

(i) *Blowpipe test.*—All nickel compounds when heated with sodium carbonate on charcoal yield grey, slightly magnetic scales of metallic nickel. If these are placed upon a strip of filter paper, dissolved by means of a few drops of nitric acid, a few drops of concentrated hydrochloric acid added and the filter paper dried by moving it back and forth in the flame or by placing it on the outside of a test-tube containing water which is heated to the boiling point, the paper acquires a green colour owing to the formation of nickelous chloride. On moistening the filter paper with ammonium hydroxide solution and adding a few drops of the dimethyl-glyoxime reagent, a red colour is produced.

(ii) *Borax bead test.*—This is coloured brown in the oxidising flame, due to the formation of nickel meta-borate $Ni(BO_2)_2$ or of the complex meta-borate $Na_2[Ni(BO_2)_4]$ (see Section **II, 1**), and grey, due to metallic nickel, in the reducing flame.

MANGANESE, Mn

Manganese is a greyish-white metal, similar in appearance to cast iron. It reacts with warm water forming manganous hydroxide and hydrogen. Dilute mineral acids and also acetic acid dissolve it with the production of manganese salts and hydrogen. Sulphur dioxide is evolved with hot concentrated sulphuric acid.

Six oxides of manganese are known: MnO, Mn_2O_3, Mn_3O_4, MnO_2, MnO_3 and Mn_2O_7. The most important compounds, the manganous salts, are derivatives of manganous oxide MnO; the manganic salts, derived from Mn_2O_3, which correspond to the ferric salts, are unstable and do not exist under ordinary analytical conditions. All the oxides dissolve in warm hydrochloric acid and hot concentrated sulphuric acid forming manganous salts, the higher oxides being reduced with the evolution of chlorine and oxygen respectively.

The two unstable acidic oxides MnO_3 and Mn_2O_7 give rise to the manganates, *e.g.*, K_2MnO_4 or K_2O,MnO_3, and permanganates, *e.g.*,

$K_2Mn_2O_8$ or K_2O,Mn_2O_7, respectively. These are discussed in Section **IV, 34.**

$$\begin{aligned} Mn &+ 2HCl &&= MnCl_2 + H_2 ; \\ MnO_2 &+ 4HCl &&= MnCl_2 + Cl_2 + 2H_2O ; \\ Mn_3O_4 &+ 8HCl &&= 3MnCl_2 + Cl_2 + 4H_2O ; \\ 2Mn_2O_3 &+ 4H_2SO_4 &&= 4MnSO_4 + O_2 + 4H_2O ; \\ 2Mn_3O_4 &+ 6H_2SO_4 &&= 6MnSO_4 + O_2 + 6H_2O ; \\ 2MnO_2 &+ 2H_2SO_4 &&= 2MnSO_4 + O_2 + 2H_2O. \end{aligned}$$

III, 26. REACTIONS OF THE MANGANOUS ION, Mn^{++}

Use a solution of manganous chloride, $MnCl_2,4H_2O$, or of manganous sulphate, $MnSO_4,5H_2O$. (Manganous compounds are usually pink in aqueous solution.)

1. **Sodium Hydroxide Solution**: white precipitate of manganous hydroxide $Mn(OH)_2$, insoluble in excess of the reagent. The precipitate rapidly oxidises on exposure to air, becoming brown; the brown compound is either manganic hydroxide, $Mn(OH)_3$, or manganous acid, H_2MnO_3 or $MnO.(OH)_2$, or perhaps a mixture of the two.

$$\begin{aligned} MnCl_2 + 2NaOH &= Mn(OH)_2 + 2NaCl ; \\ 4Mn(OH)_2 + 2H_2O + O_2 &= 4Mn(OH)_3 ; \\ 2Mn(OH)_2 + O_2 &= 2H_2MnO_3. \end{aligned}$$

2. **Ammonium Hydroxide Solution**: partial precipitation of white manganous hydroxide $Mn(OH)_2$, soluble in solutions of ammonium salts.

No precipitation takes place in the presence of ammonium salts owing to the lowering of the hydroxyl ion concentration and the consequent failure to attain the solubility product of $Mn(OH)_2$ (compare Sect. **I, 16**). On exposure to air brown manganic hydroxide or manganous acid H_2MnO_3 is precipitated from the ammoniacal solution. This is important in connexion with the separation from the Group IIIA metals. In precipitating iron, aluminium and chromium, the solution should contain a large excess of ammonium chloride, boiled to expel most of the dissolved air, then a *slight* excess of ammonium hydroxide solution added and the precipitate filtered *as quickly as possible*. Under these conditions very little manganese will be precipitated.

$$MnCl_2 + 2NH_4OH \rightleftharpoons Mn(OH)_2 + 2NH_4Cl.$$

3. **Ammonium Sulphide Solution**: pink (flesh-coloured) precipitate of hydrated manganous sulphide MnS, readily soluble in dilute acids (distinction from nickel and cobalt) and in acetic acid (distinction from nickel, cobalt and zinc). The presence of ammonium chloride assists precipitation since the sulphide when first formed is colloidal (compare Nickel, Section **III, 25,** reaction *3*). The precipitate turns brown on exposure to air owing to oxidation. Boiling with excess of ammonium sulphide solution converts the pink hydrated form into the less hydrated green sulphide $3MnS,H_2O$.

$$MnCl_2 + (NH_4)_2S + xH_2O = MnS,xH_2O + 2NH_4Cl.$$

4. **Sodium Phosphate Solution**: flesh-coloured precipitate of manganese ammonium phosphate $Mn(NH_4)PO_4,7H_2O$ in the presence of excess of ammonium hydroxide solution.

$$MnCl_2 + NH_4OH + Na_2HPO_4 + 6H_2O = Mn(NH_4)PO_4,7H_2O + 2NaCl.$$

5. **Lead Dioxide and Concentrated Nitric Acid.**—On boiling a dilute solution of a manganous salt, free from hydrochloric acid and chlorides, with lead dioxide (or red lead, which yields the dioxide in the presence of nitric acid) and a little concentrated nitric acid, diluting somewhat and allowing the suspended solid containing unattacked lead dioxide to settle, the supernatant liquid acquires a violet-red (or purple) colour due to permanganic acid. The latter is decomposed by hydrochloric acid hence chlorides should be absent.

$$5PbO_2 + 2MnSO_4 + 6HNO_3 = 2HMnO_4 + 3Pb(NO_3)_2 + 2PbSO_4 + 2H_2O.$$

6. **Ammonium or Potassium Persulphate.**—When the solid is boiled with a solution of a manganous salt in dilute sulphuric acid in the presence of a little silver nitrate solution (which acts as a catalyst), a reddish-violet solution of permanganic acid is formed. The unstable silver peroxide is probably intermediately formed and this acts as the oxidising agent.

$$2(NH_4)_2S_2O_8 + 2H_2O = 2(NH_4)_2SO_4 + 2H_2SO_4 + 2O;$$

$$4AgNO_3 + 2O + 2H_2O = 2Ag_2O_2 + 4HNO_3;$$

$$2MnSO_4 + 5Ag_2O_2 + 6HNO_3 = 2HMnO_4 + 6AgNO_3 + 2Ag_2SO_4 + 2H_2O.$$

7. **Sodium Bismuthate** ($NaBiO_3$).—When this solid is added to a *cold* solution of a manganous salt in dilute nitric acid (sp. gr. 1·13), the mixture stirred and the excess of the reagent filtered off (preferably through asbestos or glass wool), a solution of permanganic acid is produced.

$$5NaBiO_3 + 2MnSO_4 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + NaNO_3 + 2Na_2SO_4 + 7H_2O.$$

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† The spot-test technique is as follows. Place a drop of the test solution on a spot plate, add a drop of concentrated nitric acid and then

a little sodium bismuthate. The purple colour of permanganic acid appears. If the solution is so dark that the colour cannot be detected, dilute the mixture with water until the colour appears.

Sensitivity : 25 μg. Mn (in 5 c.c.). Concentration limit : 1 in 200,000.

8. **Potassium Periodate** (KIO_4).—The manganous sulphate solution is rendered strongly acid with sulphuric or nitric acid, 0·2–0·3 gram of potassium periodate added, and the solution boiled for 1 minute. A solution of permanganic acid is formed.

This reaction is more effective than tests *5*, *6* and *7*. Chlorides, however must be absent ; if present, they must be removed by evaporation with sulphuric or nitric acid before applying the test.

$$2MnSO_4 + 5KIO_4 + 3H_2O = 2HMnO_4 + 5KIO_3 + 2H_2SO_4.$$

†*9.* **Potassium Periodate—"Tetrabase" Test.**—A solution of the "tetrabase" (tetramethyl-diamino-diphenylmethane) in chloroform is employed as a sensitive test to identify very small amounts of manganese as permanganic acid. The latter oxidises the "tetrabase" to an intensely blue compound. Chromium salts should be absent for they are oxidised by periodates to chromates, which yield a similar colour with the "tetrabase."

Place a drop of the test solution on a spot plate, followed by a drop of saturated potassium periodate solution and 2 drops of a 1 per cent solution of the "tetrabase" in chloroform. A deep blue colour is formed.

Sensitivity : 0·001 μg. Mn. Concentration limit : 1 in 50,000,000.

†*10.* **Ammonium Persulphate Test.**—Manganese salts in dilute sulphuric or nitric acid solution react only on warming with persulphates with the formation of hydrated manganese dioxide. If, however, the solution contains some silver ions as catalyst, oxidation proceeds to the permanganate state :

$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O = 2MnO_4^- + 10SO_4^{--} + 16H^+.$$

Chlorides, bromides, iodides and other salts that precipitate silver should be absent, as should also compounds which will react with permanganic acid.

Place a drop of the test solution in a micro-crucible, add 1 drop of concentrated sulphuric acid and 1 drop of 0·1*N*-silver nitrate solution, and stir. Introduce a few milligrams of solid ammonium persulphate and heat gently. The characteristic colour of permanganic acid appears.

Sensitivity : 0·1 μg. Mn. Concentration limit : 1 in 500,000.

†*11.* **Formaldoxime Reagent** ($HCH = NOH$) : red colouration with alkaline solution of manganous salts. Copper gives a blue-violet colouration, but the interference can be overcome by the use of alkali cyanide. Iron is best removed before applying the test (*e.g.*, with zinc oxide or sodium acetate), although it may be rendered inactive by the addition of a tartrate. Chromium, cobalt and nickel salts give colourations with the reagent and must therefore be absent.

Place a few c.c. of the test solution, which has been rendered just alkaline with 4*N*-sodium hydroxide, into a micro test-tube and add 1 drop of the reagent. A red colouration is obtained.

Sensitivity: 0·25 μg. (in 5 c.c.). Concentration limit: 1 in 20,000,000.

The **reagent** consists of a 2·5 per cent. solution of formaldoxime in water.

Dry Tests

(i) *Borax bead test.*—The bead produced in the oxidising flame by small amounts of manganese salts is violet whilst hot and amethyst-red when cold; with larger amounts of manganese the bead is almost brown and may be mistaken for that of nickel. In the reducing flame the manganese bead is colourless whilst that due to nickel is grey.

(ii) *Fusion test.*—Fusion of any manganese compound with sodium carbonate and an oxidising agent (potassium chlorate or potassium nitrate) gives a green mass of alkali manganate. The test may be carried out either by heating upon a piece of platinum foil with potassium nitrate and sodium carbonate (if platinum foil is not available, a piece of broken porcelain may be employed), or by fusing a bead of sodium carbonate with a small quantity of the manganese compound in the oxidising flame and dipping the fused mass while hot into a little powdered potassium chlorate or nitrate and reheating (compare Section **II, 1**).

$$MnSO_4 + 2KNO_3 + 2Na_2CO_3 = Na_2MnO_4 + 2KNO_2 + Na_2SO_4 + 2CO_2.$$

$$3MnSO_4 + 2KClO_3 + 6Na_2CO_3 = 3Na_2MnO_4 + 2KCl + 3Na_2SO_4 + 6CO_2.$$

ZINC, Zn

Zinc is a bluish-white metal; it is fairly malleable and ductile at 110–150°. The pure metal dissolves very slowly in acids and in alkalis; the presence of impurities, or contact with platinum or copper, produced by the addition of a few drops of the solutions of the salts of these metals, accelerates the reaction. This explains the solubility of commercial zinc. The latter dissolves readily in dilute hydrochloric and in dilute sulphuric acid, with the evolution of hydrogen. Solution takes place with very dilute nitric acid, but no gas is evolved; with increasing concentration of acid, nitrous oxide or nitric oxide is evolved, depending upon the concentration; concentrated nitric acid has very little action owing to the very slight solubility of zinc nitrate. Sulphur dioxide is evolved with hot concentrated sulphuric acid. Zinc also dissolves in solutions of caustic alkalis with the evolution of hydrogen and the formation of zincates,

$$Zn + H_2SO_4 = ZnSO_4 + H_2;$$

$$4Zn + 10HNO_3 \quad 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O;$$

$$4Zn + 10HNO_3 \quad 4Zn(NO_3)_2 + N_2O + 5H_2O;$$

$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 2NO + 4H_2O;$$

$$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O;$$

$$Zn + 2NaOH = Na_2[ZnO_2] + H_2.$$

Only one series of salts is known; these are derivatives of the oxide ZnO.

III, 27. REACTIONS OF THE ZINC ION, Zn^{++}

Use a solution of zinc sulphate, $ZnSO_4,7H_2O$.

1. **Sodium Hydroxide Solution**: white, gelatinous precipitate of zinc hydroxide $Zn(OH)_2$, readily soluble in excess of the reagent with the formation of sodium zincate (distinction from manganese). The precipitate also dissolves in dilute acids and is therefore amphoteric.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4;$$

$$Zn(OH)_2 + 2NaOH \rightleftharpoons Na_2[ZnO_2] + 2H_2O.$$

2. **Ammonium Hydroxide Solution**: white precipitate of zinc hydroxide, readily soluble in excess of the reagent and in solutions of ammonium salts owing to the production of complex compounds. The non-precipitation of zinc hydroxide by ammonium hydroxide solution in the presence of ammonium chloride is due to the lowering of the hydroxyl ion concentration to such a value that the solubility product of $Zn(OH)_2$ is not attained (compare Section **I, 16**).

$$ZnSO_4 + 2NH_4OH \rightleftharpoons Zn(OH)_2 + (NH_4)_2SO_4;$$

$$Zn(OH)_2 + 6NH_4OH \rightleftharpoons [Zn(NH_3)_6](OH)_2 + 6H_2O.$$

3. **Ammonium Sulphide Solution**: white precipitate of zinc sulphide ZnS from neutral or alkaline solutions; it is insoluble in excess of the reagent, in acetic acid and in solutions of caustic alkalis, but dissolves in dilute mineral acids. The precipitate thus obtained is partially colloidal; it is difficult to wash and tends to run through the filter paper, particularly on washing. To obtain the zinc sulphide in a form which can be readily filtered, the precipitation is best carried out in boiling solution in the presence of excess of ammonium chloride, and the precipitate washed with dilute ammonium chloride solution containing a little ammonium sulphide.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

4. **Hydrogen Sulphide**: partial precipitation of zinc sulphide in neutral solutions; when the concentration of acid produced is about 0·3*M* (*p*H about 0·6), the sulphide ion concentration derived from the hydrogen sulphide is depressed so much by the hydrogen ion concentration from the acid that it is too low to exceed the solubility product of ZnS, and consequently precipitation ceases. Upon the addition of alkali acetate to the solution, the hydrogen ion concentration is reduced because of the formation of the feebly dissociated acetic acid, the sulphide ion concentration is correspondingly increased, and precipitation is almost complete (compare Section **I, 16**). Zinc sulphide is precipitated from solutions of alkali zincates by hydrogen sulphide.

$$ZnSO_4 + H_2S \rightleftharpoons ZnS + H_2SO_4.$$

$$2Na.C_2H_3O_2. + H_2SO_4 = 2H.C_2H_3O_2 + Na_2SO_4.$$

$$Na_2[ZnO_2] + H_2S \rightleftharpoons ZnS + 2NaOH.$$

5. **Sodium Phosphate Solution**: white precipitate of zinc ammonium phosphate $Zn(NH_4)PO_4$ in the presence of ammonium chloride; the precipitate is soluble in ammonium hydroxide solution and in dilute acids.

$$ZnSO_4 + NH_4Cl + 2Na_2HPO_4 \rightleftharpoons Zn(NH_4)PO_4 + NaH_2PO_4 + Na_2SO_4 + NaCl.$$

6. **Potassium Ferrocyanide Solution**: white precipitate of zinc ferrocyanide $Zn_2[Fe(CN)_6]$, which is converted by excess of the reagent into the less soluble zinc potassium ferrocyanide $Zn_3K_2[Fe(CN)_6]_2$.

$$2ZnSO_4 + K_4[Fe(CN)_6] = Zn_2[Fe(CN)_6] + 2K_2SO_4$$

$$3Zn_2[Fe(CN)_6] + K_4[Fe(CN)_6] = 2Zn_3K_2[Fe(CN)_6]_2.$$

The precipitate is insoluble in dilute acids, but dissolves in solutions of caustic alkalis:

$$Zn_2[Fe(CN)_6] + 8NaOH = 2Na_2[ZnO_2] + Na_4[Fe(CN)_6] + 4H_2O.$$

7. **Quinaldinic Acid Reagent** (Quinoline-α-carboxylic acid, $C_9H_6N.CO_2H$).—Upon the addition of a few drops of the reagent to a solution of a zinc salt which is faintly acid with acetic acid, a white precipitate of the zinc complex salt $Zn(C_{10}H_6NO_2)_2,H_2O$ is obtained. The precipitate is soluble in ammonium hydroxide solution and in mineral acids, but is reprecipitated on neutralisation. Copper, cadmium, uranium, iron and chromium ions give precipitates with the reagent and should be absent. Cobalt, nickel and manganese ions have no effect. This is an extremely sensitive test for zinc ions, and is a useful confirmatory test for zinc isolated from the Group IIIB separation. The reagent is, however, expensive.

The *reagent* is prepared by neutralising 1 gram of quinaldinic acid with sodium hydroxide solution and diluting to 100 c.c.

8. **Mercuri-thiocyanate—Copper Sulphate Reagent.**—The solution is treated with ammonium phosphate solution (to suppress the action of any iron which may be present) and acidified with dilute acetic or sulphuric acid* ; 0·5 c.c. of 0·1% copper sulphate solution is added, followed by 2 c.c. of "ammonium mercuric thiocyanate" solution. A violet precipitate is obtained. The test is rendered still more (sensitive to 10 μg. of zinc) by boiling the mixture for 1 minute, cooling, and shaking with a little amyl alcohol ; the violet precipitate collects at the interface.

The *ammonium mercuri-thiocyanate solution* is prepared by dissolving 8 grams of mercuric chloride and 9 grams of ammonium thiocyanate in 100 c.c. of water.

†*9.* **Mercuri-thiocyanate—Cobalt Acetate Reagent.**—Zinc salts react with ammonium mercuri-thiocyanate $(NH_4)_2[Hg(CNS)_4]$ to give a white crystalline precipitate ; with small amounts of zinc this separates very slowly because of supersaturation phenomena :

$$Zn^{++} + [Hg(CNS)_4]^{--} = Zn[Hg(CNS)_4].$$

Cobalt salts react similarly to give a blue crystalline compound $Co[Hg(CNS)_4]$. If a very dilute solution of a cobalt salt, from which a precipitate would otherwise separate very slowly, is treated with a solution containing zinc ions, a blue precipitate is formed at once even when the amount of zinc added is very small. The production of mixed crystals of the mercuri-thiocyanates of cobalt and zinc eliminates the supersaturation. If iron is present, a red colouration is produced ; this disappears when a little alkali fluoride is added.

Place a drop of the slightly acid (hydrochloric acid) test solution on a spot plate, add a drop of a 0·1 per cent solution of cobalt acetate, a drop of the reagent and a few milligrams of solid sodium or ammonium fluoride. Rub the plate gently with a glass rod for about 15 seconds. A blue precipitate is formed within 2 minutes : in the absence of zinc precipitation first commences after 2 to 3 minutes. A blank test should be performed.

Sensitivity : 0·2–0·5 μg. Zn. Concentration limit : 1 in 100,000.

The preparation of the ammonium mercuri-thiocyanate reagent is described in reaction *8.*

† *10.* **Potassium Ferricyanide—Orange IV (or Tropaeolin 00) Test.**—Potassium ferricyanide slowly oxidises the azo-dyestuff Orange IV with a change of colour and the formation of potassium ferrocyanide. If the ferrocyanide formed is removed by zinc ions as the sparingly-soluble, white zinc ferrocyanide, the oxidation proceeds rapidly and

* Alternatively, 2–3 c.c. of 85% phosphoric acid may be employed.

the white zinc ferrocyanide is deeply coloured by the oxidation product. Only those ions (copper, cobalt, nickel, manganese, etc.) which form coloured precipitates with potassium ferrocyanide interfere.

Place 1 drop of a 0·01 per cent aqueous solution of Orange IV and 1 drop of 1·5*N*-sulphuric acid in a microtest-tube, add 3–5 drops of a freshly prepared 2 per cent solution of potassium ferricyanide and shake. A red colour is produced. Add a drop of the test solution. A green colouration appears.

† *11.* **Rinmann's Green Test.**—Rinmann's green is most probably composed of mixed crystals of zinc oxide and cobaltous oxide and is generally obtained (see **Dry Tests** below) by heating the oxides or salts, such as carbonates or nitrates, that are readily converted into the oxides. An excess of cobaltous oxide must be avoided for it leads to a red-brown colouration ; oxidation to cobaltic oxide produces a darkening of colour. Suitable experimental conditions are obtained by converting the zinc into the cobalticyanide $Zn_3[Co(CN)_6]$: ignition of the latter leads to zinc oxide and cobaltous oxide in the optimum ratio of 3 : 2, whilst the carbon from the filter paper (see below) prevents the formation of cobaltic oxide.

Soak a quantitative filter paper in a solution containing 4 g. of potassium cobalticyanide and 1 g. of potassium chloride in 100 c.c. of water, and dry it at 100°C or at room temperature (this **potassium cobalticyanide paper** is yellow and will keep). Place a drop of the test solution containing about 5 per cent of free nitric acid on to a small strip (1 cm.) of the paper, dry it over a flame and ignite in a small crucible. Transfer the ash to a spot plate : it will be green.

Sensitivity: 0·6 μg. Zn (in 0·002 c.c.). Concentration limit : 1 in 3,000.

All other metals must be removed, but the test is applicable in the presence of twice the amount of aluminium.

Dry Tests

Blowpipe test.—Compounds of zinc when heated upon charcoal with sodium carbonate give an incrustation of the oxide, which is yellow when hot and white when cold. The metal cannot be isolated owing to its volatility and subsequent oxidation. If the incrustation is moistened with a drop of cobalt nitrate solution and again heated, a green mass (Rinmann's green), consisting either of cobalt zincate $CoZnO_2$ or, more probably, of a solid solution of cobalt oxide in zinc oxide, is obtained.

An alternative method is to soak a piece of ashless filter paper in the zinc salt solution, add one drop of cobalt nitrate solution and to ignite in a crucible or in a coil of platinum wire. The residue is coloured green.

DETECTION AND SEPARATION OF THE METALS IN THE ZINC GROUP (GROUP IIIB)

As in previous groups, the student should obtain from the teacher, or prepare for himself, a mixture of some or all of the simple soluble salts of the metals of this group. It is assumed that all the metals of the earlier groups are either absent or have been removed. Add excess of ammonium chloride solution or 1–2 grams of solid ammonium chloride, heat to boiling and add ammonium sulphide solution

III, 28. Table XXI.—Analysis of the Zinc Group (Group IIIB)

<table>
<tr><td colspan="3">The precipitate may contain CoS, NiS, MnS and ZnS, together with finely-divided sulphur. Wash the ppt. with 1% NH_4Cl solution containing a little ammonium sulphide solution. Transfer the ppt. to a small beaker and stir with cold, very dilute HCl (1 volume conc. acid : 10 volumes of water) and filter after 2–3 minutes.</td></tr>
<tr><td rowspan="2">Residue. If black, may contain CoS and NiS.
Test residue with borax bead.
Blue bead.
Co present.
Dissolve residue in a mixture of 2·5 c.c. of 10% NaOCl solution and 0·5 c.c. of dilute HCl. Add 1 c.c. of dilute HCl and boil until Cl_2 is expelled. Cool and dilute to about 4 c.c. Divide into 2 equal parts.
1. Add 1 c.c. of amyl alcohol, 2–3 g. of solid NH_4CNS, and shake.
Amyl alcohol layer coloured blue.
Co present.
2. Add a little NH_4Cl solution, NH_4OH solution until faintly alkaline, and then excess of dimethyl glyoxime reagent.
Red ppt.
Ni present.</td><td colspan="2">Filtrate. May contain $MnCl_2$ and $ZnCl_2$.
Boil until H_2S is removed (test with lead acetate paper), cool, add excess of NaOH solution, and filter cold.</td></tr>
<tr><td>Residue. White, $Mn(OH)_2$, turning brown owing to oxidation. Dissolve the ppt. in 5–10 c.c. of concentrated HNO_3, add 1 gram of Pb_3O_4, boil for 1 minute, and allow to settle. Purple solution of $HMnO_4$.
Mn present.
OR Fuse residue with Na_2CO_3 and KNO_3 on porcelain or Pt. foil.
Green mass.
Mn present.</td><td>Filtrate.
May contain Na_2ZnO_2.
Pass H_2S for 1 minute.
White ppt. of ZnS.
Zn present.
Confirm by Rinmann's green test.</td></tr>
</table>

slowly until no further precipitation occurs. The presence of excess of ammonium sulphide solution should be avoided as this will tend to produce a colloidal solution of nickel sulphide (and sometimes of zinc sulphide) which passes through the filter paper giving a dark-coloured, turbid solution. This danger is increased if the ammonium sulphide solution has not been freshly prepared and may therefore contain the polysulphide $(NH_4)_2S_x$. It is usually better to add excess of ammonium hydroxide solution after the addition of ammonium chloride, heat to boiling and to pass hydrogen sulphide until precipitation is complete [Table on p. 215].

THE CALCIUM GROUP (GROUP IV)

BARIUM, STRONTIUM AND CALCIUM

This group comprises the three alkaline earth metals; they are distinguished from the metals of the preceding groups by the fact that their salts are not precipitated by hydrochloric acid, hydrogen sulphide or ammonium sulphide, and are characterised by their precipitation with ammonium carbonate solution in the presence of ammonium chloride and ammonium hydroxide solutions.

BARIUM, Ba

Barium is a silver-white, malleable and ductile metal, which is stable in dry air. It reacts with water at the ordinary temperature forming barium hydroxide and liberating hydrogen. The metal is soluble in acids with the evolution of hydrogen.

III, 29. REACTIONS OF THE BARIUM ION, Ba^{++}

Use a solution of barium chloride, $BaCl_2,2H_2O$.

1. **Ammonium Hydroxide Solution**: no precipitate of barium hydroxide because of its relatively high solubility*. If the alkaline solution is exposed to the atmosphere, some carbon dioxide is absorbed and a turbidity, due to barium carbonate, is produced.

2. **Ammonium Carbonate Solution**§: white precipitate of barium carbonate, soluble in acetic acid and in dilute mineral acids.

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl.$$

3. **Ammonium Oxalate Solution**: white precipitate of barium oxalate BaC_2O_4, slightly soluble in water (0·09 g. per litre; S.P. $1{\cdot}7 \times 10^{-7}$), but readily dissolved by hot dilute acetic acid (distinction from calcium) and by mineral acids.

$$BaCl_2 + (NH_4)_2C_2O_4 = BaC_2O_4 + 2NH_4Cl.$$

4. **Dilute Sulphuric Acid**‡: heavy, white, finely-divided precipitate of barium sulphate $BaSO_4$, practically insoluble in water (2·5 milligrams per litre ; S.P. $1{\cdot}2 \times 10^{-10}$), almost insoluble in dilute acids and in ammonium sulphate solution, and appreciably soluble in boiling concentrated sulphuric acid. By precipitation in boiling solution or preferably in the presence of ammonium acetate, a more readily filterable form is obtained.

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* A slight turbidity is due to small amounts of ammonium carbonate often present in the reagent.

§ Or a solution of any soluble carbonate.

‡ Or a solution of any soluble sulphate.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

$$BaSO_4 + H_2SO_4\ (\text{conc.}) \rightleftharpoons Ba(HSO_4)_2.$$

If barium sulphate is boiled with a concentrated solution of sodium carbonate, partial transformation into the less soluble barium carbonate occurs in accordance with the equation :

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

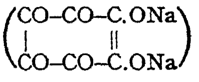
Owing to the reversibility of the reaction, the transformation is incomplete. If the mixture is filtered and washed (thus removing the sodium sulphate), and the residue boiled with a fresh volume of sodium carbonate solution, more of the barium sulphate will be converted into barium carbonate. By repetition of this process, practically all of the sulphate can be converted into the corresponding carbonate. The carbonate may be dissolved in acids ; this process therefore provides a method for bringing insoluble sulphates into solution. A more expeditious method of obtaining the same result is to fuse the barium sulphate with 4–6 times its weight of anhydrous sodium carbonate ; the maximum concentration of carbonate is thus obtained and the reaction proceeds almost to completion in one operation (compare Law of Mass Action, Section **I, 9**). The melt is allowed to cool, extracted with boiling water and filtered ; the residue of barium carbonate can then be dissolved in the appropriate acid. It has been stated that by boiling barium sulphate with at least 15 times its equivalent weight of 1–2*M* sodium carbonate solution, 99% is converted into barium carbonate in 1 hour.

5. **Saturated Calcium Sulphate Solution** : immediate white precipitate of barium sulphate. A similar but more trustworthy result is obtained with saturated strontium sulphate solution.

$$CaSO_4 + BaCl_2 = BaSO_4 + CaCl_2.$$

6. **Potassium Chromate Solution** : yellow precipitate of barium chromate $BaCrO_4$, practically insoluble in water (3·8 milligrams per litre ; S.P. $2{\cdot}3 \times 10^{-10}$) and in dilute acetic acid (distinction from strontium and calcium), but readily soluble in mineral acids (compare Sections **I, 17** and **IV, 23**).

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2KCl.$$

† *7.* **Sodium Rhodizonate Reagent**  $\left(\begin{array}{l} CO\text{–}CO\text{–}C.ONa \\ |\qquad\qquad \| \\ CO\text{–}CO\text{–}C.ONa \end{array}\right)$: reddish-brown precipitate of the barium salt of rhodizonic acid in neutral solution. Calcium salts do not interfere : strontium salts react like those of barium, but only the precipitate due to the former is completely soluble in dilute hydrochloric acid. Other elements, *e.g.*, those

precipitated by hydrogen sulphide and by ammonium sulphide, should be absent. The reagent should be confined to testing for elements in Group IV (calcium group).

Place a drop of the neutral or faintly acid test solution upon drop-reaction paper and add a drop of the reagent. A brown or reddish-brown spot is obtained.

Sensitivity: 0·25 μg. Ba. Concentration limit: 1 in 200,000.

The **reagent** consists of a 5 per cent aqueous solution of sodium rhodizonate. It does not keep well so that only small quantities should be prepared at a time.

In the **presence of strontium** the reddish-brown stain of barium rhodizonate is treated with 0·5*N*-hydrochloric acid; the strontium rhodizonate dissolves, whilst the barium derivative is converted into the brilliant red acid salt. The reaction is best carried out on drop-reaction paper as above.

Treat the reddish-brown spot with a drop of 0·5*N*-hydrochloric acid when a bright red stain is formed if barium is present. If barium is absent, the spot disappears.

Sensitivity: 0·5 μg. Ba in the presence of 50 times the amount of Sr. Concentration limit: 1 in 90,000.

Dry Test

Flame colouration.—Barium salts, when heated in the non-luminous Bunsen flame, impart a yellowish-green colour to the flame. Since most barium salts, with the exception of the chloride, are non-volatile, the platinum wire is moistened with concentrated hydrochloric acid before being dipped into the substance. The sulphate is first reduced to the sulphide in the reducing flame, then moistened with concentrated hydrochloric acid, and re-introduced into the flame.

STRONTIUM, Sr

Strontium is a silver-white, malleable and ductile metal. Its properties are similar to those of barium.

III, 30. REACTIONS OF THE STRONTIUM ION, Sr^{++}

Use a solution of strontium chloride, $SrCl_2,6H_2O$.

1. **Ammonium Hydroxide Solution**: no precipitate.

2. **Ammonium Carbonate Solution**: white precipitate of strontium carbonate $SrCO_3$, less soluble in water than barium carbonate.

3. **Dilute Sulphuric Acid** *: white precipitate of strontium sulphate $SrSO_4$, very sparingly soluble in water (0·110 g. per litre; S.P. $3{\cdot}6 \times 10^{-7}$), insoluble in ammonium carbonate solution even on boiling (distinction from calcium) and slightly soluble in boiling hydrochloric acid. It is almost

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*** Or a solution of any soluble sulphate.**

completely converted into the corresponding carbonate by boiling with a concentrated solution of sodium carbonate.

$$SrSO_4 + Na_2CO_3 \rightleftharpoons SrCO_3 + Na_2SO_4.$$

4. **Saturated Calcium Sulphate Solution** : white precipitate of strontium sulphate, formed slowly in the cold but more rapidly on boiling (distinction from barium).

5. **Ammonium Oxalate Solution** : white precipitate of strontium oxalate, sparingly soluble in water (0·066 g. per litre ; S.P. $1{\cdot}4 \times 10^{-7}$) and in acetic acid, but soluble in mineral acids.

6. **Potassium Chromate Solution** : yellow precipitate of strontium chromate $SrCrO_4$ from concentrated solutions ; the precipitate is appreciably soluble in water (1·2 grams per litre) and in acetic acid. No precipitation therefore occurs in dilute solutions nor from concentrated solutions containing acetic acid (distinction from barium).

†*7.* **Sodium Rhodizonate Reagent** : reddish-brown precipitate of strontium rhodizonate in neutral solution. The test is applied to the elements of Group IV (calcium group). Barium reacts similarly and a method for the detection of barium in the presence of strontium has already been described (Section **III, 29,** reaction *7*). To detect strontium in the presence of barium, the latter is converted into the insoluble barium chromate. Barium chromate does not react with sodium rhodizonate, but the more soluble strontium chromate reacts normally.

If **barium is absent,** place a drop of the neutral test solution on drop-reaction paper or on a spot plate, and add a drop of the reagent. A brownish-red colouration or precipitate is produced.

Sensitivity : 0·45 μg. Sr.

If **barium is present,** proceed as follows. Impregnate some quantitative filter paper or drop-reaction paper with a saturated solution of potassium chromate, and dry it. Place a drop of the test solution on this paper and, after a minute, place 1 drop of the reagent on the moistened spot. A brownish-red spot or ring is formed.

Sensitivity : 4 μg. Sr in the presence of 80 times the amount of Ba. Concentration limit : 1 in 13,000.

For further details of the reagent, see under Barium, Section **III, 29,** reaction *7*.

Dry Test

Flame Colouration.—Volatile strontium compounds, especially the chloride, impart a characteristic carmine-red colour to the non-luminous Bunsen flame (see remarks under Barium).

CALCIUM, Ca

Calcium, like the other elements of this group, is a silver-white metal and possesses similar properties. It is, however, only slightly attacked by concentrated nitric acid.

III, 31. REACTIONS OF THE CALCIUM ION, Ca^{++}

Use a solution of calcium chloride, $CaCl_2,6H_2O$.

1. **Ammonium Hydroxide Solution**: no precipitate. The result is similar to that for barium ions.

2. **Ammonium Carbonate Solution**: white amorphous precipitate of calcium carbonate $CaCO_3$, which becomes crystalline on boiling. The precipitate is soluble in water containing excess of carbonic acid, due to the formation of the soluble bicarbonate. This remark applies also to the carbonates of strontium and barium.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

3. **Dilute Sulphuric Acid** *: white precipitate of calcium sulphate $CaSO_4,2H_2O$ from concentrated solutions. The precipitate is appreciably soluble in water (2·0 g. per litre at 25°; S.P. $2{\cdot}3 \times 10^{-4}$), is more soluble in acids than either strontium or barium sulphates, and is readily soluble in hot ammonium sulphate solution owing to the formation of a complex salt (distinction from strontium).

$$CaSO_4 + (NH_4)_2SO_4 = (NH_4)_2[Ca(SO_4)_2].$$

4. **Saturated Calcium Sulphate Solution**: no precipitate (difference from strontium and barium).

5. **Ammonium Oxalate Solution**: white precipitate of calcium oxalate CaC_2O_4,H_2O, immediately from concentrated solutions and slowly from dilute solutions. Precipitation is facilitated by making the solution alkaline with ammonium hydroxide solution. The precipitate is practically insoluble in water (8 milligrams per litre at 20°; S.P. $3{\cdot}8 \times 10^{-9}$), insoluble in acetic acid, but readily dissolved by mineral acids (compare Section **I, 17**).

6. **Potassium Chromate Solution**: no precipitate in dilute solutions (solubility 23 g. per litre) nor from concentrated solutions containing free acetic acid.

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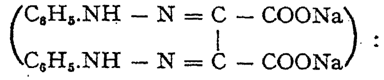
* Of a solution of any soluble sulphate.

7. **Potassium Ferrocyanide Solution**: white precipitate of calcium potassium ferrocyanide $CaK_2[Fe(CN)_6]$ is produced by excess of the reagent. The test is more sensitive in the presence of excess of ammonium chloride solution; a white precipitate of calcium potassium ammonium ferrocyanide of variable composition is formed (distinction from strontium and barium).

$$CaCl_2 + K_4[Fe(CN)_6] = CaK_2[Fe(CN)_6] + 2KCl.$$

†*8.* **Sodium Dihydroxytartrate Osazone Reagent**



$$\left(\begin{array}{c} C_6H_5.NH - N = C - COONa \\ \qquad\qquad\quad | \\ C_6H_5.NH - N = C - COONa \end{array}\right):$$

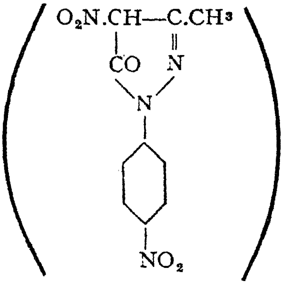
yellow sparingly-soluble precipitate of the calcium salt. All other metals, with the exception of alkali and ammonium salts, must be absent. Magnesium does not interfere provided its concentration does not exceed 10 times that of the calcium.

Place a drop of the neutral test solution on a black spot plate or upon a black watch glass, and add a tiny fragment of the solid reagent. If calcium is absent, the reagent dissolves completely. The presence of calcium is revealed by the formation over the surface of the liquid of a white film which ultimately separates as a dense precipitate.

Sensitivity: 0·01 μg. Ca. Concentration limit: 1 in 5,000,000.

The reagent is useful *inter alia* for the rapid differentiation between tap and distilled water: a positive result is obtained with a mixture of 1 part of tap water and 30 parts of distilled water.

†*9.* **Picrolonic Acid (or 1:p-Nitrophenyl-3-methyl-4-nitro-5-pyrazolone) Reagent**: characteristic rectangular crystals of calcium picrolonate $Ca(C_{10}H_7O_5N_4)_2,8H_2O$ in neutral or acetic acid solutions. Strontium and barium give precipitates but of different crystalline form. Numerous elements, including copper, lead, thorium, iron, aluminium, cobalt, nickel and barium, interfere.



Place a drop of the neutral test solution (or acidified with acetic acid) in the depression of a *warm* spot plate and add 1 drop of a saturated aqueous solution of picrolonic acid. Characteristic rectangular crystals are produced.

Sensitivity: 100 μg. (in 5 c.c.). Concentration limit: 1 in 50,000. The sensitivity is 0·01 μg (in 0·01 c.c.) under the microscope.

Dry Test

Flame Colouration.—Volatile calcium compounds impart a yellowish-red colour to the Bunsen flame (see remarks under Barium).

DETECTION AND SEPARATION OF THE METALS IN THE CALCIUM GROUP (GROUP IV)

It is assumed that the metals of Groups I to IIIB have been removed as already described, or that only metals of the alkaline earth group are present. As in previous group separations, the student should prepare or obtain from the teacher a solution containing some or all of the simple salts of the metals of Group IV. The filtrate from Group IIIB, if employed, should be concentrated to a small volume before applying the tests contained in Table XXII.

III, 32. Table XXII.—Analysis of the Calcium Group (Group IV)

Add 2–3 c.c. of NH_4OH solution, heat nearly to boiling and add excess of $(NH_4)_2CO_3$ solution until precipitation is complete. Filter and discard the filtrate.

Residue. May contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Dissolve the ppt. in hot dilute acetic acid. Test a small portion for barium by heating to boiling and adding a little K_2CrO_4 solution ; if a yellow ppt. forms, treat the whole of the hot solution with a *slight* excess of K_2CrO_4 solution (*i.e.*, until the solution just assumes an orange tint), and filter.

If no ppt. is formed with the K_2CrO_4 reagent (Ba absent), boil the remainder of the solution for 1 minute to expel CO_2, cool under running water, and use the solution (*A*) in testing for Sr and Ca.

Residue. Yellow : $BaCrO_4$. Wash with a little hot water. Dissolve the ppt. in 2–3 c.c. of concentrated HCl and apply the flame test.
Apple-green flame.
Ba present.

Filtrate. Render alkaline with NH_4OH solution and add excess of $(NH_4)_2CO_3$ reagent. A white ppt. indicates the presence of $SrCO_3$ and/or $CaCO_3$. Wash. Dissolve the ppt. in warm dilute acetic acid, boil to expel CO_2, and cool in running water (solution *B*). Divide solution *A* or *B* into 2 unequal parts. Render the larger portion alkaline with NH_4OH solution, add 10–15 c.c. of boiling, saturated $(NH_4)_2SO_4$ solution, and allow to stand for 5–10 minutes, keeping the solution warm. Filter.

Residue. $SrSO_4$ and, possibly, a little $CaSO_4$. Place the filter paper in a crucible, heat until the paper has charred, add a few drops of concentrated HCl, and apply the flame test.
Crimson flame.
Sr present.

Filtrate. Add a little NH_4OH solution, followed by $(NH_4)_2C_2O_4$ solution in slight excess. Boil and allow to stand for 5 minutes. White ppt. of CaC_2O_4, insoluble in acetic acid.
Ca present.

Filter off the ppt., and confirm Ca by flame test ; brick-red flame.

Note. If Sr is absent, use the smaller portion of *A* or *B* for the NH_4OH–$(NH_4)_2C_2O_4$ test.

THE ALKALI GROUP (GROUP V)
MAGNESIUM, SODIUM, POTASSIUM (LITHIUM) AND AMMONIUM

The metals of this group are not precipitated by the earlier group reagents. Sodium, potassium and lithium belong to the alkali metal group ; ammonium is included in this group since its compounds resemble those of the alkali metals, particularly those of potassium. Magnesium, although associated with the alkaline earths in the periodic table, is incorporated in this group because its carbonate is not precipitated by ammonium carbonate solution in the presence of ammonium chloride.

MAGNESIUM, Mg

Magnesium is a white, malleable and ductile metal which burns in air or oxygen with a brilliant white light, forming the oxide MgO and a little nitride Mg_3N_2. The metal is slowly decomposed by water at the ordinary temperature but rapidly at 100°. It is readily soluble in acids liberating hydrogen. The salts are derived from the basic oxide MgO.

III, 33. REACTIONS OF THE MAGNESIUM ION, Mg^{++}

Use a solution of magnesium sulphate, $MgSO_4,7H_2O$.

1. **Ammonium Hydroxide Solution**: partial precipitation of white, gelatinous magnesium hydroxide $Mg(OH)_2$, very sparingly soluble in water (12 milligrams per litre; S.P. $3{\cdot}4 \times 10^{-11}$), but readily soluble in solutions of ammonium salts.

$$MgSO_4 + 2NH_4OH \rightleftharpoons Mg(OH)_2 + (NH_4)_2SO_4.$$

As the reaction progresses, the concentration of the ammonium ions, due to the dissociation of the completely ionised ammonium salt, increases and consequently the concentration of the hydroxyl ions decreases owing to the common ion effect (compare Section **I, 14**). The small hydroxyl ion concentration, already low, is decreased still further so that much of the magnesium salt remains in solution. In the presence of a sufficient concentration of ammonium salts, the ionisation of the ammonium hydroxide is depressed to such an extent that the solubility product of $Mg(OH)_2$ is not exceeded (compare Section **I, 15**); hence magnesium is not precipitated by ammonium hydroxide solution in the presence of ammonium chloride or other ammonium salts.

2. **Sodium Hydroxide Solution**: white precipitate of magnesium hydroxide, insoluble in excess of the reagent, but readily soluble in solutions of ammonium salts.

3. **Ammonium Carbonate Solution**: white precipitate of basic magnesium carbonate, often only on boiling or on long standing. No precipitate is obtained in the presence of ammonium salts since the latter, by virtue of the common ion effect, reduces the carbonate ion concentration to so low a value that the solubility product of $MgCO_3$ ($2{\cdot}6 \times 10^{-5}$) is not attained.

When only *small* quantities of the alkaline earth metals are present, ammonium carbonate solution may fail to precipitate or will only partially precipitate the carbonates of these metals if ammonium salts of strong acids are present. The solubility products of $CaCO_3$, $SrCO_3$ and $BaCO_3$ are $1{\cdot}7 \times 10^{-8}$, $4{\cdot}6 \times 10^{-9}$ and $1{\cdot}9 \times 10^{-9}$ respectively. In the presence of, say, ammonium chloride, the hydrogen ions derived from the latter as a result of hydrolysis (Sect. **I, 40**) will combine with the carbonate ions from the ammonium carbonate yielding the slightly dissociated HCO_3^- ion. Consequently the CO_3^{--} concentration may become so low that the solubility products of the alkaline earth carbonates may not be exceeded, if the metal ion concentration is small. If, however, the metal ion concentration is appreciable, the influence of the ammonium salts will be small and the alkaline earth carbonates will be precipitated. Incidentally this provides an explanation of the slight solubility of the alkaline earth carbonates in ammonium chloride solution.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+;$$
$$H^+ + CO_3^{--} \rightleftharpoons HCO_3^-.$$

4. **Sodium Carbonate Solution** : white voluminous precipitate of basic carbonate $4MgCO_3,Mg(OH)_2,5H_2O$ or $[Mg(MgCO_3)_4](OH)_2$, insoluble in solutions of bases, but soluble in acids and in solutions of ammonium salts.

$$5MgSO_4 + 5Na_2CO_3 + H_2O = 4MgCO_3,Mg(OH)_2 + 5Na_2SO_4 + CO_2.$$

5. **Sodium Phosphate Solution** : white crystalline precipitate of magnesium ammonium phosphate $Mg(NH_4)PO_4$ in the presence of ammonium chloride (to prevent the precipitation of magnesium hydroxide) and ammonium hydroxide solutions, very sparingly soluble in water (8·6 milligrams per litre; S.P. $2{\cdot}5 \times 10^{-13}$), soluble in acetic acid and in mineral acids. The precipitate separates slowly from dilute solutions because of its tendency to form supersaturated solutions; this may usually be overcome by cooling and by rubbing the test-tube or beaker beneath the surface of the liquid with a glass rod.

A white flocculent precipitate of magnesium hydrogen phosphate $MgHPO_4$ is produced in *neutral* solutions.

$$MgSO_4 + Na_2HPO_4 + NH_4OH = Mg(NH_4)PO_4 + Na_2SO_4 + H_2O.$$
$$MgSO_4 + Na_2HPO_4 = MgHPO_4 + Na_2SO_4.$$

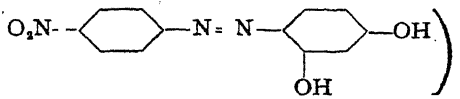
6. **Diphenyl-carbazide Reagent** ($C_6H_5.NH.NH.CO.NH.NH.C_6H_5$).—The magnesium salt solution is treated with sodium hydroxide solution—a precipitate of magnesium hydroxide will be formed—then with a few drops of the diphenylcarbazide reagent and the solution filtered. On washing the precipitate with hot water, it will be seen to have acquired a violet-red colour, due to the formation of a complex salt. Metals of Groups II and III interfere and should therefore not be present.

The *reagent* is prepared by dissolving 0·2 gram of diphenylcarbazide in 10 c.c. of glacial acetic acid and diluting to 100 c.c. with rectified spirit.

7. **8-Hydroxy-quinoline Reagent or "Oxine" Reagent** ($C_9H_6N.OH$).—When a magnesium salt solution, containing ammonium chloride and ammonium hydroxide solution, is treated with 1–2 c.c. of the reagent, a yellow precipitate of the complex salt, $(C_9H_6N.O)_2Mg,4H_2O$, is obtained. All other metals, except those of the alkalis, must be absent.

The *reagent* is prepared by dissolving 5 g. of the solid in 100 c.c. of rectified spirit.

8. **para-Nitrobenzene-azo-resorcinol** (or **Magneson I**)



Reagent.—This test depends upon the adsorption of the reagent, which is a dyestuff, whereby a blue lake (compare Section **I, 43**) is produced. Two c.c. of the test solution, slightly acid with hydrochloric acid, is treated with 1 drop of the reagent and sufficient *N*-sodium hydroxide solution to render the solution strongly alkaline, say 2-3 c.c. A blue precipitate appears. This is an excellent confirmatory test in macro-analysis, but it is essential to perform a blank test with the reagents, which frequently yield a blue colouration. For this reason a blue precipitate should be looked for. All metals, except those of the alkalis, must be absent. Ammonium salts reduce the sensitivity of the test.

The *reagent* (for macro-analysis) consists of a 0·5 per cent solution of *p*-nitrobenzene-azo-resorcinol in 0·25*N*-sodium hydroxide.

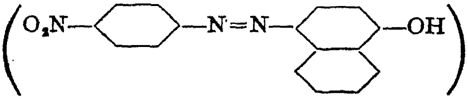
† The spot-test technique is as follows. Place a drop of the test solution on a spot plate and add 1–2 drops of the reagent. It is essential that the solution be strongly alkaline; the addition of 1 drop of *N*-sodium hydroxide may be advisable. According to the concentration of magnesium a blue precipitate is formed or the reddish-violet reagent assumes a blue colour. A comparative test on distilled water should be carried out.

Sensitivity: 0·5 μg. Mg. Concentration limit: 1 in 100,000.

Filter or drop-reaction paper should not be used.

The **reagent** is prepared by dissolving 0·001 g. of the dyestuff in 100 c.c. of *N*-sodium hydroxide.

An alternative agent is **para-nitrobenzene-azo-α-naphthol** or **Magneson II.** It yields the same colour changes as magneson I, but has the advantage that it is more sensitive (sensitivity: 0·2 μg. Mg; concentration limit: 1 in 250,000) and its tinctorial power is less so that the blank test is not so deeply coloured. Its mode of use is identical with that described above for magneson I.



† *9.* **Titan Yellow Reagent.**—Titan yellow (also known as Clayton Yellow and Thiazole Yellow) is a water-soluble yellow dyestuff. It is

adsorbed by magnesium hydroxide producing a deep red colour or precipitate. Barium and calcium do not react but intensify the red colour. All elements of Groups I to IIIB should be removed before applying the test.

Place a drop of the test solution on a spot plate, introduce a drop of reagent and a drop of 0·1*N* sodium hydroxide. A red colour or precipitate is produced.

Sensitivity : 1·5 μg. Mg. Concentration limit : 1 in 33,000.

The **reagent** consists of a 0·1 per cent aqueous solution of titan yellow.

†*10*. **Quinalizarin* Reagent** : blue precipitate or cornflower-blue colouration with magnesium salts. The colouration can be readily distinguished from the blue-violet colour of the reagent. Upon the addition of a little bromine water, the colour disappears (difference from beryllium). The alkaline earth metals and aluminium do not interfere under the conditions of the test, but all elements of Groups I to IIIB should be removed. Phosphates and large amounts of ammonium salts decrease the sensitivity of the reaction.

Place a drop of the test solution and a drop of distilled water in adjacent cavities of a spot plate and add 2 drops of the reagent to each. If the solutions are acid, they will be coloured yellowish-red by the reagent. Add 2*N*-sodium hydroxide until the colour changes to violet and a further excess to increase the volume by 25 to 50 per cent. A blue precipitate or colouration appears. The blank test has a blue-violet colour.

Sensitivity : 0·25 μg. Mg. Concentration limit : 1 in 200,000.

The **reagent** is prepared by dissolving 0·01–0·02 g. of quinalizarin in 100 c.c. of alcohol. Alternatively, a 0·05 per cent solution in 0·1*N*-sodium hydroxide may be used.

Dry Test

Blowpipe test.—All magnesium compounds when ignited on charcoal in the presence of sodium carbonate are converted into white magnesium oxide, which glows brightly when hot. Upon moistening with a drop or two of cobalt nitrate solution and reheating strongly, a pale pink mass is obtained.

POTASSIUM, K

Potassium is a soft, silver-white metal. It remains unchanged in dry air, but is rapidly oxidised in moist air, becoming covered first with a blue film. The metal decomposes water violently, evolving hydrogen and burning with a violet flame. Potassium is usually kept under solvent naphtha. The salts are derived from the normal oxide K_2O.

III, 34. REACTIONS OF THE POTASSIUM ION, K^+

Use a solution of potassium chloride, KCl.

1. **Sodium Cobaltinitrite Solution** ($Na_3[Co(NO_2)_6]$) : yellow precipitate of potassium cobaltinitrite $K_3[Co(NO_2)_6]$, insoluble in dilute acetic acid solution. The precipitate forms immediately in concentrated solutions and slowly in dilute solutions; precipitation may be accelerated by warming. Ammonium salts give a similar precipitate and must therefore be completely eliminated before applying the test. In alkaline solutions, a brown or black precipitate of cobaltic hydroxide $Co(OH)_3$ is obtained. Iodides and other reducing agents interfere and should be removed before applying the test.

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*See under Aluminium, Section **III, 21**, reaction *10*.

$$Na_3[Co(NO_2)_6] + 3KCl\,(\text{excess}) = K_3[Co(NO_2)_6] + 3NaCl.$$
$$Na_3[Co(NO_2)_6] + 2KCl = K_2Na[Co(NO_2)_6] + 2NaCl.$$

2. **Tartaric Acid Solution** ($H_2.C_4H_4O_6$)* : white crystalline precipitate of potassium acid tartrate $KH.C_4H_4O_6$ from concentrated solutions. The precipitate is slightly soluble in water (3·2 g. per litre; S.P. $3{\cdot}0 \times 10^{-4}$), insoluble in 50% alcohol, soluble in mineral acids, and also in solutions of alkalis with the formation of the normal salts, *e.g.*, $K_2.C_4H_4O_6$. Precipitation is accelerated by vigorous agitation of the solution, by scratching the sides of the vessel with a glass rod and by adding alcohol. Ammonium salts yield a similar precipitate and must be absent.

$$KCl + H_2.C_4H_4O_6 = KH.C_4H_4O_6 + HCl;$$
$$KCl + NaH.C_4H_4O_6 = KH.C_4H_4O_6 + NaCl.$$

3. **Perchloric Acid Solution** ‡ ($HClO_4$) : white crystalline precipitate of potassium perchlorate $KClO_4$ from not too dilute solutions. The precipitate is slightly soluble in water (3·2 g. and 198 g. per litre at 0° and 100° respectively) and practically insoluble in absolute alcohol. *The alcoholic solution should not be heated as a dangerous explosion may result.* This reaction takes place in the presence of ammonium salts.

$$HClO_4 + KCl = KClO_4 + HCl.$$

4. **Chloroplatinic Acid Solution** ($H_2[PtCl_6]$) : yellow crystalline precipitate of potassium chloroplatinate $K_2[PtCl_6]$ from concentrated solutions; in dilute solutions, precipitation takes place slowly on standing, but may be hastened by cooling and by rubbing the sides of the vessel with a glass rod. The precipitate is slightly soluble in water, but is almost insoluble in 75% alcohol. Ammonium salts give a similar precipitate and must be absent.

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* Or preferably saturated sodium hydrogen tartrate solution.

‡ 20% strength. An equivalent result is obtained by the use of sodium perchlorate solution.

$$2KCl + H_2[PtCl_6] = K_2[PtCl_6] + 2HCl.$$

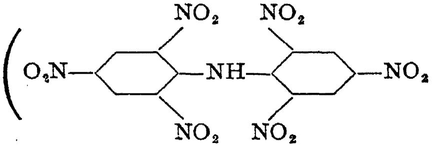
The *reagent* is prepared by dissolving 2·7 grams of the hydrated chloroplatinic acid $H_2[PtCl_6],6H_2O$ in 10 c.c. of water. Owing to its expensive character, only small quantities should be employed and all precipitates placed in the platinum residues bottle.

† *5*. **Sodium Cobaltinitrite-Silver Nitrate Test.**—This is a modification of reaction *1* and is applicable to halogen-free solutions. Precipitation of potassium salts with sodium cobaltinitrite and silver nitrate solution gives the compound $K_2Ag[Co(NO_2)_6]$, which is less soluble than the corresponding sodium compound $K_2Na[Co(NO_2)_6]$ and hence the test is more sensitive. Lithium, thallium and ammonium salts must be absent for they give precipitates with sodium cobaltinitrite solution.

Place a drop of the neutral or acetic acid test solution on a black spot plate, and add a drop of 0·05 per cent silver nitrate solution and a small amount of finely-powdered sodium cobaltinitrite. A yellow precipitate or turbidity appears.

Sensitivity: 1 μg. K. Concentration limit: 1 in 50,000. If silver nitrate solution is not added, the sensitivity is 4 μg. K.

† *6*. **Dipicrylamine (or Hexanitro-diphenylamine) Reagent**



the hydrogen atom of the NH group is replaceable by metals; the sodium salt is soluble in water to yield a yellow solution. With solutions of potassium salts, the latter gives a crystalline orange-red precipitate of the potassium derivative. The test is applicable in the presence of 80 times as much sodium and 130 times as much lithium. Ammonium salts should be removed before applying the test.

Place a drop of the neutral test solution upon drop-reaction paper and immediately add a drop of the slightly alkaline reagent. An orange-red spot is obtained, which is unaffected by treatment with 1–2 drops of $2N$-hydrochloric acid.

Sensitivity: 3 μg. K. Concentration limit: 1 in 10,000.

The **reagent** is prepared by dissolving 0·2 g. of dipicrylamine in 20 c.c. of boiling $0{\cdot}1N$-sodium carbonate and filtering the cooled liquid.

Dry Test

Flame colouration.—Potassium compounds, preferably the chloride, colour the non-luminous Bunsen flame violet (lilac). The yellow flame produced by small quantities of sodium obscures the violet colour, but by viewing the flame through two thicknesses of cobalt blue glass, the yellow sodium rays are absorbed and the reddish-violet potassium flame becomes visible. A solution of chrome alum (310 g. per litre), 3 cms. thick, also makes a good filter.

SODIUM, Na

Sodium is a silver-white, soft metal. It oxidises rapidly in moist air and is therefore kept under solvent naphtha or xylene. The metal reacts violently with water forming sodium hydroxide and evolving hydrogen. The salts are derived from the monoxide Na_2O.

III, 35. REACTIONS OF THE SODIUM ION, Na^+

Use a solution of sodium chloride, NaCl.

1. **Magnesium Uranyl Acetate Solution** : yellow, crystalline precipitate of sodium magnesium uranyl acetate $NaMg(UO_2)_3(C_2H_3O_2)_9,9H_2O$ from concentrated solutions. The addition of about one third volume of alcohol helps the precipitation.

$$NaCl + 3UO_2(C_2H_3O_2)_2 + Mg(C_2H_3O_2)_2 + H.C_2H_3O_2 \\ = NaMg(UO_2)_3(C_2H_3O_2)_9 + 9H_2O.$$

The *reagent* is prepared by warming together a mixture of 20 g. of crystalline uranyl acetate $UO_2(C_2H_3O_2)_2,2H_2O$, 66 g. of crystalline magnesium acetate $Mg(C_2H_3O_2)_2,4H_2O$, 25 c.c. of glacial acetic acid and 175 c.c. of water until most of the solid has dissolved. Allow to stand for 24 hours and filter.

2. **Potassium Dihydrogen Antimonate Solution** (KH_2SbO_4)*: white, crystalline precipitate of sodium dihydrogen antimonate NaH_2SbO_4 from not too dilute solutions. The solution must be neutral or weakly alkaline ; acids and solutions of ammonium salts of strong acids give a white, amorphous precipitate of antimonic acid H_3SbO_4. Precipitation is accelerated by rubbing the test-tube or beaker under the surface of the liquid with a glass rod. All metals, other than those of the alkalis, must be absent.

$$KH_2SbO_4 + NaCl = NaH_2SbO_4 + KCl.$$
$$KH_2SbO_4 + HCl = H_3SbO_4 + KCl.$$

The *reagent* is prepared by adding 5·5 g. of potassium antimonate K_3SbO_4 to 250 c.c. of boiling water, boiling until nearly all the salt has dissolved, cooling rapidly, adding 9 c.c. of 10% potassium hydroxide solution, and filtering after standing overnight.

$$2K_3SbO_4 + 4H_2O \rightleftharpoons 2KH_2SbO_4 + 4KOH.$$

3. **Chloroplatinic Acid, Tartaric Acid or Sodium Cobaltinitrite Solution** : no precipitate with solutions of sodium salts.

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* Formerly called potassium pyroantimonate and formulated $K_2H_2Sb_2O_7$.

† *4.* **Zinc Uranyl Acetate Reagent.**—As a delicate test for sodium, the zinc uranyl acetate reagent is sometimes preferred to that employing magnesium uranyl acetate. The yellow crystalline sodium zinc uranyl acetate $NaZn(UO_2)_3(C_2H_3O_2)_9,9H_2O$ is obtained. The reaction is fairly selective for sodium. The sensitivity of the reaction is affected by copper, mercury, cadmium, aluminium, cobalt, nickel, manganese, zinc, calcium, strontium, barium and ammonium when present in concentrations exceeding 5 g. per litre; potassium and lithium salts are precipitated if their concentration in solution exceeds 5 g. and 1 g. per litre respectively.

Place a drop of the neutral test solution on a black spot plate or upon a black watch glass, add 8 drops of the reagent, and stir with a glass rod. A yellow cloudiness or precipitate forms.

Sensitivity: 12·5 μg. Na. Concentration limit: 1 in 4,000.

The **reagent** is prepared as follows. Dissolve 10 g. of uranyl acetate in 6 g. of 30 per cent acetic acid, warming if necessary, and dilute with water to 50 c.c. (solution *a*). In a separate vessel stir 30 g. of zinc acetate with 3 g. of 30 per cent acetic acid and dilute with water to 50 c.c. (solution *b*). Mix the two solutions *a* and *b*, and add a small quantity of sodium chloride. Allow to stand for 24 hours, and filter from the precipitated sodium zinc uranyl acetate.

Dry Test

Flame colouration.—The non-luminous Bunsen flame is coloured an intense yellow by vapours of sodium salts. The colour is not visible when viewed through two thicknesses of cobalt blue glass. Minute quantities of sodium salts give this test, and it is only when the colour is intense and persistent that appreciable quantities of sodium are present.

III, 36. REACTIONS OF THE AMMONIUM ION, NH_4^+

Use a solution of ammonium chloride, NH_4Cl.

1. **Sodium Hydroxide Solution**: ammonia gas is evolved on warming. This may be identified (*a*) by its odour (cautiously smell the vapour after removing the test-tube or small beaker from the flame); (*b*) by the formation of white fumes of ammonium chloride when a glass rod moistened with concentrated hydrochloric acid is held in the vapour; (*c*) by its turning moistened red litmus paper blue or turmeric paper brown; (*d*) by its ability to turn filter paper moistened with mercurous nitrate solution black (this is the most trustworthy test‡); and (*e*) filter paper moistened with a solution of manganous sulphate and hydrogen peroxide gives a brown colour, due to the oxidation of the manganese by the alkaline solution thus formed.

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‡ Arsine, however, blackens mercurous nitrate paper, and must therefore be absent.

$$NH_4Cl + NaOH = NH_3 + H_2O + NaCl;$$

$$2Hg_2(NO_3)_2 + 4NH_3 + H_2O = \underbrace{OHg_2.NH_2.NO_3 + 2Hg}_{\text{black}} + 3NH_4NO_3;$$

$$2MnSO_4 + H_2O_2 + 4NH_4OH = 2Mn(OH)_3 + 2(NH_4)_2SO_4.$$

2. **Nessler's Reagent**: brown precipitate (formula $O.Hg_2.NH_2.I$*, or brown or yellow colouration, is produced according to the amount of ammonia or of ammonium ions. The test is an extremely delicate one and will detect the traces of ammonia present in drinking water. All metals, except those of the alkalis, must be absent.

The *reagent* is prepared by dissolving 10 g. of potassium iodide in 10 c.c. of water, adding saturated mercuric chloride solution (60 g. per litre) in small quantities at a time, with shaking, until a slight permanent precipitate is formed, then adding 80 c.c. of 9*M* potassium hydroxide solution and diluting to 200 c.c. Allow to stand overnight and decant the clear liquid. The reagent thus consists of an alkaline solution of potassium mercuri-iodide K_2HgI_4.

An alternative method for the *preparation of the reagent* is as follows. Dissolve 23 g. of mercuric iodide and 16 g. of potassium iodide in water and make up the volume to 100 c.c.; add 100 c.c. of 6*N*-sodium hydroxide. Allow to stand for 24 hours, and decant the solution from any precipitate that may have formed. The solution should be kept in the dark. For delicate work, ammonia-free water should be used.

$$2KI + HgI_2 = K_2[HgI_4];$$

$$2K_2[HgI_4] + NH_3 + 3KOH = O.Hg_2.NH_2.I + 7KI + 2H_2O.$$

† The spot-test technique is as follows. Mix a drop of the test solution with a drop of concentrated sodium hydroxide solution on a watch glass. Transfer a micro-drop of the resultant solution or suspension to drop-reaction paper and add a drop of Nessler's reagent. A yellow or orange-red stain or ring is produced.

Sensitivity: 0·3 μg. NH_3 (in 0·002 c.c.).

A better procedure is to employ the technique described under the manganous nitrate—silver nitrate reagent in reaction *8* below. A drop of Nessler's solution is placed on the glass knob of the apparatus. After the reaction is complete, the drop of the reagent is touched with a piece of drop-reaction or quantitative filter paper when a yellow colouration will be apparent.

Sensitivity: 0·025 μg. NH_3.

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* M. L. Nichols and C. O. Willits (1934) have shown that the formula is more probably $NH_2Hg_2I_3$.

3. **Sodium Cobaltinitrite Solution** ($Na_3[Co(NO_2)_6]$) : yellow precipitate of ammonium cobaltinitrite $(NH_4)_3[Co(NO_2)_6]$, similar to that produced by potassium ions.

$$3NH_4Cl + Na_3[Co(NO_2)_6] = (NH_4)_3[Co(NO_2)_6] + 3NaCl.$$

4. **Chloroplatinic Acid Solution** ($H_2[PtCl_6]$) : yellow, crystalline precipitate of ammonium chloroplatinate $(NH_4)_2[PtCl_6]$, similar to that of the corresponding potassium salt, but differing from it in being decomposed by warming with sodium hydroxide solution with the evolution of ammonia gas.

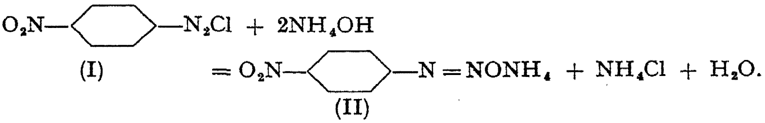
$$2NH_4Cl + H_2[PtCl_6] = (NH_4)_2[PtCl_6] + 2HCl;$$
$$(NH_4)_2[PtCl_6] + 2NaOH = Na_2[PtCl_6] + 2NH_3 + 2H_2O.$$

5. **Saturated Sodium Hydrogen Tartrate Solution** ($NaH.C_4H_4O_6$)* : white precipitate of ammonium acid tartrate $NH_4.H.C_4H_4O_6$, similar to but slightly more soluble than the corresponding potassium salt, from which it is distinguished by the evolution of ammonia gas on being heated with sodium hydroxide solution.

$$NaH.C_4H_4O_6 + NH_4Cl = NH_4.H.C_4H_4O_6 + NaCl.$$

6. **Perchloric Acid or Sodium Perchlorate Solution** : no precipitate (distinction from potassium).

† *7.* **para-Nitrobenzene-diazonium Chloride Reagent.**—The reagent (I) yields a red colouration (due to II) with an ammonium salt in the presence of sodium hydrozide solution.



Place a drop of the neutral or slightly acid test solution on a spot plate, followed by a drop of the reagent and a fine granule of calcium oxide. A red zone forms round the calcium oxide. A blank test should be carried out on a drop of water.

Sensitivity : 0·7 μg. Concentration limit : 1 in 75,000.

The **reagent** (sometimes known as **Riegler's solution**) is prepared as follows. Dissolve 1 g. of *p*-nitraniline in 2 c.c. of concentrated hydrochloric acid and 20 c.c. of distilled water (warming may be necessary) and dilute with 160 c.c. of water. Cool, add 20 c.c. of 2–5 per cent sodium nitrite solution with vigorous shaking. Continue the shaking until all dissolves. The reagent becomes turbid on keeping, but can be employed again after filtering.

† *8.* **Ammonia-Formation Test.**—This is a modification of reaction *1* as adapted to delicate analysis. The apparatus is shown in Fig. 36 and

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* Or, less effectively, tartaric acid solution.

consists of a small glass tube of 1 c.c. capacity, which can be closed with a small ground-glass stopper carrying a small glass hook at the lower end.

Place a drop of the test solution or a little of the solid in the micro-test-tube, and add a drop of 2*N*-sodium hydroxide solution. Fix a small piece of red litmus paper on the glass hook and insert the stopper into position. Warm to 40°C for 5 minutes. The paper assumes a **blue colour.**

Sensitivity: 0·01 μg. NH_3. Concentration limit: 1 in 5,000,000.

Cyanides should be absent, for they give ammonia with alkalis:

$$KCN + H_2O = HCOOK + NH_3.$$

If, however, a little mercuric oxide or a mercuric salt is added, the alkali-stable mercuric cyanide $Hg(CN)_2$ is formed and the interfering effect of cyanides is largely eliminated.

An alternative method for carrying out the test is to employ the **manganous nitrate—silver nitrate reagent.** Upon treating a neutral solution of manganous and silver salts with alkalis (*e.g.*, that produced from ammonia), a black precipitate is formed:

$$Mn^{++} + 2Ag^+ + 4OH^- = MnO_2 + 2Ag + 2H_2O.$$

The sensitivity can be increased by treating the resultant precipitate with an acetic acid solution of benzidine whereupon the manganese dioxide oxidises the benzidine to a blue oxidation product.

Use the apparatus shown in Fig. 34 or in Fig. 35. Place a drop of the test solution and a drop of 2*N*-sodium hydroxide in the micro test-tube; also place a drop of the reagent on the glass knob of the stopper and close the apparatus. Heat at 40°C for 5 minutes. Wash the drop of the reagent on to a piece of quantitative filter paper when a black or grey fleck will become apparent; this turns blue upon treatment with a solution of benzidine (the latter is prepared by dissolving 0·05 g. of benzidine or its hydrochloride in 10 c.c. of glacial acetic acid, diluting to 100 c.c. with water, and filtering).

Sensitivity: 0·005 μg. NH_3. Concentration limit: 1 in 10,000,000.

The manganous nitrate—silver nitrate reagent is prepared thus. Dissolve 2·87 g. of manganous nitrate in 40 c.c. of water and filter: add a solution of 1·69 g. of silver nitrate in 40 c.c. of water, and dilute the mixture to 100 c.c. Neutralise the acid formed by hydrolysis by adding dilute alkali dropwise until a black precipitate is formed and filter. Keep the reagent in a dark bottle.

Dry Test

All ammonium salts are either volatilised or decomposed when heated to just below red heat. In some cases, where the acid is volatile, the vapours recombine on cooling to form a sublimate of the salt, *e.g.*, ammonium chloride.

LITHIUM, Li‡

Lithium is a silver-white metal; it is the lightest metal known

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‡ The analytical chemistry of this element is included in Group V as a knowledge of its reactions is required by students of pharmacy.

(density 0·534 at 0°) and floats upon petroleum. It oxidises on exposure to air, and reacts with water forming lithium hydroxide and liberating hydrogen, but the reaction is not so vigorous as with sodium and potassium. The metal dissolves in acids with the formation of salts. The salts are derived from the monoxide Li_2O.

Some of the salts, notably the chloride LiCl and the chlorate $LiClO_3$, are very deliquescent. The solubilities of the hydroxide LiOH (113 g. per litre at 10°), carbonate Li_2CO_3 (13·1 g. per litre at 13°), the phosphate Li_3PO_4 (0·30 g. per litre at 25°) and the fluoride LiF (2·7 g. per litre at 18°) are less than the corresponding sodium and potassium salts, and in this respect lithium resembles the alkaline earth metals.

III, 37. REACTIONS OF THE LITHIUM ION, Li^+

Use a solution of lithium chloride, LiCl.

1. **Sodium Phosphate Solution** : partial precipitation of lithium phosphate Li_3PO_4 in neutral solutions ; the precipitate is more readily obtained from dilute solutions on boiling. Precipitation is almost complete in the presence of sodium hydroxide solution. The precipitate is more soluble in ammonium chloride solution than in water (distinction from magnesium).

$$3LiCl + Na_2HPO_4 + NaOH = Li_3PO_4 + 3NaCl + H_2O.$$

Upon boiling the precipitate with barium hydroxide solution, it passes into solution as lithium hydroxide (difference from magnesium).

2. **Ammonium Carbonate Solution** : white precipitate of lithium carbonate Li_2CO_3 from concentrated solutions and in the presence of ammonium hydroxide solution. No precipitation occurs in the presence of excess of ammonium chloride.

$$2LiCl + (NH_4)_2CO_3 \rightleftharpoons Li_2CO_3 + 2NH_4Cl.$$

3. **Ammonium Fluoride Solution.**—A white gelatinous precipitate of lithium fluoride LiF is slowly formed in ammoniacal solution.

$$LiCl + NH_4F = LiF + NH_4Cl.$$

4. **Tartaric Acid or Sodium Cobaltinitrite or Chloroplatinic Acid Solution** : no precipitate (distinction from potassium).

† *5.* **Potassium Periodate-Ferric Chloride Test.**—Ferric salts react with periodates to yield a precipitate of a complex ferric periodate, which dissolves in excess of alkali and of periodate. The resultant alkaline

solution of the ferric periodate complex is a selective reagent for lithium, since it alone of the alkali metals gives a yellowish-white, sparingly-soluble precipitate with the reagent. Ammonium salts, all metals of Groups I to IV, and magnesium should be absent.

Place a drop of the neutral or alkaline test solution in a micro test-tube, and add several drops of saturated sodium chloride solution and 2 drops of the reagent. Carry out a blank test with a drop of distilled water simultaneously. Dip both tubes for 15–20 seconds in water at 40°–50°C. A yellowish-white turbidity appears ; the blank test remains clear.

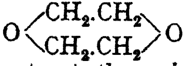
Sensitivity : 0·1 μg. Li. Concentration limit : 1 in 500,000.

The **reagent** is prepared by dissolving 2 g. of potassium periodate in 10 c.c. of freshly-prepared 2*N*-potassium hydroxide, diluting with water to 50 c.c., adding 3 c.c. of 10 per cent ferric chloride solution, and diluting to 100 c.c. with 2*N*-potassium hydroxide. The reagent is stable.

Dry Test

Flame colouration.—Lithium compounds impart a carmine-red colour to the non-luminous Bunsen flame. The colour is masked by the presence of considerable amounts of sodium salts, but becomes visible when observed through two thicknesses of cobalt glass.

The most distinctive test utilises the spectroscope ; the spectrum consists of a beautiful red line at 6708Å.

To separate lithium from the other alkali metals, they are all converted into the chlorides (by evaporation with concentrated hydrochloric acid, if necessary), evaporated to dryness, and the residue extracted with absolute alcohol which dissolves the lithium chloride only. Better solvents are dry dioxan (diethylene dioxide,  $O\left\langle\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\right\rangle O$) and dry acetone. Upon evaporation of the extract, the residue of lithium chloride is (*a*) subjected to the flame test, and (*b*) precipitated as the phosphate after dissolution in water and adding sodium hydroxide solution.

DETECTION AND SEPARATION OF THE METALS OF THE ALKALI GROUP (GROUP V)

The metals of this group are not precipitated by the earlier group reagents. It is assumed that the elements of Groups I to IV have been removed as already described, or that only metals of Group V are present. The student should, as in previous groups, prepare for himself or obtain from the teacher, a solution containing some or all of the simple salts of the metals of the group. The filtrate from Group IV, if employed, should be concentrated to half bulk, treated with 1–2 c.c. each of ammonium oxalate solution and ammonium sulphate solution, heated to boiling and filtered, if necessary ; this removes traces of alkaline earth metals which may be present and would interfere with the tests for magnesium (compare Section **III, 38,** reaction *3*).

III, 38. Table XXIII.—Analysis of the Alkali Group (Group V)

Divide the solution into two unequal parts.

Smaller portion.	*Larger portion.*
Add NH_4OH solution (also NH_4Cl solution if not already present), then Na_2HPO_4 solution. Shake vigorously, cool, scrape walls of test-tube with a glass rod and allow to stand. White crystalline ppt. of $Mg(NH_4)PO_4$. **Mg present.** *Confirmatory test.* Filter off ppt. and dissolve it in a few c.c. of hot dilute HCl, add a few drops of "magneson" reagent, followed by excess of NaOH solution. Blue precipitate confirms Mg.	Evaporate to dryness in a porcelain basin and heat to dull redness until no more fumes of ammonium salts are evolved. If no residue is obtained, Na and K are absent. If a residue is obtained, add 2–3 c.c. of water, filter from any solid magnesium compound, divide filtrate into two parts (*a*) and (*b*). (*a*) Add magnesium uranyl acetate reagent and shake. Yellow crystalline ppt. **Na present.** Confirm by flame test; persistent yellow flame. (*b*) Add sodium cobaltinitrite solution and a few drops of dilute acetic acid, preferably on a watch glass. Yellow precipitate. **K present.** Confirm by flame test; view through two thicknesses of cobalt glass.

Test for ammonium by boiling original substance with sodium hydroxide solution; odour of ammonia, and vapour turns mercurous nitrate paper black. **Ammonium present.**

CHAPTER IV

REACTIONS OF THE ACID RADICALS OR ANIONS

IV, 1. The methods available for the detection of acid radicals or anions are not as systematic as those which have been described in the previous chapter for cations. No really satisfactory scheme has yet been proposed which permits of the separation of the common acid radicals into major groups, and the subsequent unequivocal separation of each group into its independent constituents. It must however be mentioned that it is possible to separate the anions into major groups dependent upon the solubilities of the silver salts, of the calcium or barium salts, and of the nickel salts* ; these, moreover, can only be regarded as useful in giving an indication of the limitations of the method and for the confirmation of the results obtained by the simpler methods to be described below. For this reason their discussion is deferred until Section **V, 17** in connexion with the complete systematic detection of acid radicals.

The following *scheme of classification* has been found to work well in practice ; it is not a rigid one since some of the acid radicals belong to more than one of the subdivisions, and, furthermore, it has no theoretical basis. Essentially the processes employed may be divided into (*A*) those involving the identification by volatile products obtained on treatment with acids, and (*B*) those dependent upon reactions in solution. Class (*A*) is subdivided into (i) gases evolved with dilute hydrochloric acid or dilute sulphuric acid, and (ii) gases or vapours evolved with concentrated sulphuric acid. Class (*B*) is subdivided into (i) precipitation reactions, and (ii) oxidation and reduction in solution.

This leads to the following classification.

CLASS A

(i) *Gases evolved with dilute hydrochloric acid or dilute sulphuric acid.*

Carbonate, bicarbonate, sulphite, thiosulphate, sulphide, nitrite, hypochlorite and cyanate.

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* See, for example, Treadwell-Hall, *Qualitative Analysis*, Volume I, 1932, p. 479 ; McAlpine and Soule, *Qualitative Chemical Analysis*, 1933, p. 537.

(ii) *Gases or acid vapours evolved with concentrated sulphuric acid.*

These include those of (i) with the addition of the following :—fluoride, chloride, bromide, iodide, nitrate, chlorate, perchlorate, bromate, iodate, borate,* ferrocyanide, ferricyanide, thiocyanate, formate, acetate, oxalate, tartrate and citrate.

CLASS B

(i) *Precipitation reactions.*

Sulphate, persulphate§, phosphate, phosphite, hypophosphite, arsenate, arsenite, silicate, fluosilicate, salicylate, benzoate and succinate.

(ii) *Oxidation and reduction in solution.*

Manganate, permanganate, chromate and dichromate.

The reactions of all these acid radicals or anions will be systematically studied in the following pages. Elementary students may omit those marked with one asterisk. For convenience the reactions of certain organic acids are grouped together ; these include acetates, formates, oxalates, tartrates, citrates, salicylates, benzoates and succinates. It may be pointed out that acetates, formates, salicylates, benzoates and succinates all belong to another group ; all give a characteristic colouration or precipitate upon the addition of ferric chloride solution to a neutral solution.

IV, 2. REACTIONS OF CARBONATES, CO_3^{--}

Solubility.—All normal carbonates, with the exception of those of the alkali metals and of ammonium, are insoluble in water. The acid carbonates or bi-carbonates of calcium, strontium, barium, magnesium and possibly of iron exist in aqueous solution ; they are formed by the action of excess of carbonic acid upon the normal carbonates either in aqueous solution or suspension and are decomposed on boiling the solutions.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

The bicarbonates of the alkali metals are soluble in water, but are less soluble than the corresponding normal carbonates.

Use sodium carbonate, $Na_2CO_3,10H_2O$.

1. **Dilute Hydrochloric Acid**‡ : decomposition with effervescence, due to the evolution of carbon dioxide, which may be detected by its property of rendering a lime water (or baryta water) turbid. Some natural carbonates, such as magnesite $MgCO_3$, siderite $FeCO_3$ and dolomite $(Ca,Mg)CO_3$, do not react appreciably in the cold ; they must be finely powdered and the reaction mixture warmed.

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* This is often included in Class B, (i).

§ Strictly speaking persulphates should be grouped with Class *B*, (ii), but are best studied together with sulphates.

‡ Or any other dilute mineral acid.

The lime water or baryta water test is best carried out in the apparatus shown in Fig. 43. The solid substance is placed in the test-tube or small distilling flask (10–25 c.c. capacity), dilute hydrochloric acid added and the cork immediately replaced. The gas which is evolved (warming may be necessary) is passed into lime water or baryta water contained in the test-tube ; the production of a turbidity indicates the presence of a carbonate. It must be remembered that with prolonged passage of carbon dioxide, the turbidity slowly disappears as a result of the formation of a soluble bicarbonate. Any acid which is " stronger," *i.e.*, has a higher ionisation constant, than of carbonic acid (K_1) will displace it from its salts, especially on warming. The weak hydrocyanic acid, boric acid and hydrogen sulphide do not decompose carbonates.

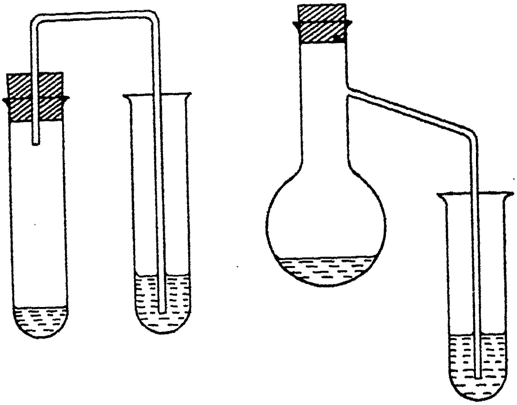

Fig. 43.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2 ;$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

2. **Barium Chloride or Calcium Chloride Solution** : white precipitate of barium carbonate $BaCO_3$ or calcium carbonate $CaCO_3$ with solutions of *normal* carbonates. The precipitate is soluble in mineral acids and in carbonic acid.

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl.$$

3. **Silver Nitrate Solution** : white precipitate of silver carbonate Ag_2CO_3 with solutions of normal carbonates, soluble in ammonium hydroxide solution and in nitric acid.

The precipitate becomes yellow upon addition of excess of the reagent, and is partly decomposed on boiling with water into brown silver oxide Ag_2O and carbon dioxide.

$$Na_2CO_3 + 2AgNO_3 = Ag_2CO_3 + 2NaNO_3.$$

† *4.* **Sodium Carbonate-Phenolphthalein Test.**—This test depends upon the fact that phenolphthalein is turned pink by soluble carbonates and colourless by soluble bicarbonates. Hence if the carbon dioxide liberated by dilute acids from carbonates is allowed to come into contact with phenolphthalein solution coloured pink by sodium carbonate solution, it may be identified by the decolourisation which takes place :

$$CO_2 + Na_2CO_3 + H_2O = 2NaHCO_3.$$

The concentration of the sodium carbonate solution must be such as not to be decolourised under the conditions of the experiment by the carbon dioxide in the atmosphere.

Place 1–2 drops of the test solution (or a small quantity of the test solid) in the apparatus shown in Fig. 34, and place a drop of the sodium carbonate-phenolphthalein reagent on the knob of the stopper. Add 3–4 drops of 2*N*-sulphuric acid and insert the stopper into position. The drop is decolourised either immediately or after a short time according to the quantity of carbon dioxide formed. Perform a blank test in a similar apparatus.

Sensitivity : 4μg. CO_2 (in 2 drops of solution). Concentration limit : 1 in 12,500.

The **reagent** is prepared by mixing 1 c.c. of 0·1*N*-sodium carbonate with 2 c.c. of a 0·5 per cent solution of phenolphthalein and 10 c.c. of water.

Sulphides, sulphites, thiosulphates, cyanides, cyanates, fluorides, nitrates and acetates interfere. The sulphur-containing anions can be quantitatively oxidised to sulphates by hydrogen peroxide :

$$Na_2S + 4H_2O_2 = N_2SO_4 + 4H_2O.$$

$$Na_2SO_3 + H_2O_2 = Na_2SO_4 + H_2O.$$

$$Na_2S_2O_3 + 4H_2O_2 = Na_2SO_4 + H_2SO_4 + 3H_2O.$$

The modified procedure in the presence of these anions is therefore to stir a drop of the test solution with 2 drops of " 20–40 volume " hydrogen peroxide, then to add 2 drops of 2*N*-sulphuric acid, and to continue as above. Cyanides are rendered innocuous by treating the test solution with 4 drops of a saturated solution of mercuric chloride, followed by 2 drops of sulphuric acid, etc. ; the slightly dissociated mercuric cyanide is formed.

IV, 3. Tests for bicarbonates.—The following tests distinguish carbonates from bicarbonates.

(i) To a cold solution of a bicarbonate, *e.g.*, sodium bicarbonate $NaHCO_3$, add a solution of magnesium sulphate. No precipitate is formed in the cold since magnesium bicarbonate $Mg(HCO_3)_2$ is soluble in water. Boil the solution : a white precipitate of magnesium carbonate $MgCO_3$, which may be contaminated with some of the basic carbonate, is produced. Solutions of carbonates give a white precipitate of magnesium carbonate with magnesium sulphate solution in the cold.

$$2NaHCO_3 + MgSO_4 = Mg(HCO_3)_2 + Na_2SO_4.$$

$$Mg(HCO_3)_2 \rightleftharpoons MgCO_3 + CO_2 + H_2O.$$

$$MgSO_4 + K_2CO_3 = MgCO_3 + K_2SO_4.$$

(ii) Boil a solution of a bicarbonate. Carbon dioxide is evolved which may be identified by the lime water test.

(iii) Add mercuric chloride solution to a solution of a bicarbonate. No precipitate is formed. Normal carbonates yield a reddish-brown precipitate of basic carbonate $Hg_4O_3.CO_3$ in the cold.

$$4Na_2CO_3 + 4HgCl_2 = Hg_4O_3.CO_3 + 8NaCl + 3CO_2.$$

(iv) Heat some solid sodium bicarbonate in a dry test-tube; carbon dioxide is evolved. The residue evolves carbon dioxide upon treatment with dilute mineral acid.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

(v) **To test for bicarbonate in the presence of a carbonate,** use is made of the fact that calcium bicarbonate $Ca(HCO_3)_2$ is soluble in water and is converted into calcium carbonate $CaCO_3$ by the addition of ammonia solution. Add excess of calcium chloride solution to precipitate the carbonate, filter and treat the clear filtrate with ammonia solution. A white precipitate or cloudiness is obtained if a bicarbonate is present

IV, 4. REACTIONS OF SULPHITES, SO_3^{--}

Solubility.—Only the sulphites of the alkali metals and of ammonium a soluble in water; the sulphites of the other metals are either difficultly solub or insoluble in water. The bisulphites of the alkali metals are soluble in the bisulphites of the alkaline earth metals are known only in solution

Use sodium sulphite, $Na_2SO_3,7H_2O$.*

1. **Dilute Hydrochloric or Dilute Sulphuric Acid**: the solid salt is decomposed, more rapidly on warming, with the evolution of sulphur dioxide, which may be identified (i) by its suffocating odour of burning sulphur, (ii) by the green colouration produced when filter paper moistened with acidified potassium dichromate solution is held over the mouth of the test-tube, and (iii) by the blue colour produced when filter paper moistened with potassium iodate solution and starch solution is held in the vapour.

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* Unless otherwise indicated, in this and all subsequent reactions of the anions the aqueous solutions should be employed.

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O.$$

$$2KIO_3 + 5SO_2 + 4H_2O = I_2 + 2KHSO_4 + 3H_2SO_4.$$

2. **Barium Chloride or Strontium Chloride Solution** : white precipitate of the sulphite $BaSO_3$ or $SrSO_3$, readily soluble in dilute hydrochloric acid. On standing, the precipitate is slowly oxidised to the sulphate and is then insoluble in dilute mineral acids ; this change is rapidly affected by warming with bromine water or a little concentrated nitric acid or with hydrogen peroxide. The solubilities at 18° of the sulphites of calcium, strontium and barium are respectively 1·25 gr., 0·033 g. and 0·022 g. per litre.

$$Na_2SO_3 + BaCl_2 = BaSO_3 + 2NaCl.$$

3. **Silver Nitrate Solution** : white crystalline precipitate of silver sulphite Ag_2SO_3, soluble in excess of the reagent forming the complex salt, sodium argenti-sulphite $Na[AgSO_3]$. The precipitate is also soluble in ammonium hydroxide solution and in dilute nitric acid. On boiling a solution of the complex salt or an aqueous suspension of the precipitate, grey metallic silver is precipitated.

$$Na_2SO_3 + 2AgNO_3 = 2NaNO_3 + Ag_2SO_3 ;$$

$$Ag_2SO_3 + Na_2SO_3 = 2Na[AgSO_3] ;$$

$$2Na[AgSO_3] = Na_2SO_4 + SO_2 + 2Ag.$$

4. **Potassium Permanganate Solution*** : decolourised owing to the formation of solutions of potassium and manganous sulphates.

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O.$$

5. **Potassium Dichromate Solution‡** : a green solution containing a chromic salt is produced. (Equation under reaction *1.*)

6. **Lead Acetate Solution** : white precipitate of lead sulphite $PbSO_3$, readily soluble in cold dilute nitric acid, and precipitating white lead sulphate on boiling (distinction from thiosulphate).

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* Acidified with dilute sulphuric acid.

‡ Acidified with dilute sulphuric acid.

$$Pb(C_2H_3O_2)_2 + Na_2SO_3 = PbSO_3 + 2Na.C_2H_3O_2.$$

$$PbSO_3 + O = PbSO_4.$$

7. **Iodine Solution** : decolourised.

$$H_2SO_3 + I_2 + H_2O \rightleftharpoons 2HI + H_2SO_4.$$

8. **Nascent Hydrogen.**—Add the solution of the sulphite to a test-tube containing zinc and dilute sulphuric acid; hydrogen sulphide is evolved which may be detected by holding some lead acetate paper at the mouth of the test-tube (see Section **IV, 6,** reaction *1*).

$$H_2SO_3 + 6H = H_2S + 3H_2O.$$

9. **Lime Water.**—This test is carried out by adding dilute hydrochloric acid to the solid sulphite, and bubbling the evolved sulphur dioxide through lime water (Fig. 43) ; a white precipitate of calcium sulphite $CaSO_3$ is formed. The precipitate dissolves on prolonged passage of the gas, due to the formation of the soluble calcium bisulphite $Ca(HSO_3)_2$. A turbidity is also produced by carbonates ; the sulphur dioxide must therefore be first removed when testing for the latter. This may be effected by adding potassium dichromate solution to the test-tube before acidifying The dichromate oxidises and destroys the sulphur dioxide without affecting the carbon dioxide (compare Section **IV, 2**).

$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O$$

$$CaSO_3 + SO_2 + H_2O \rightleftharpoons Ca(HSO_3)_2.$$

† *10.* **Malachite Green Test.**—Dilute solutions of triphenylmethane dyestuffs, such as malachite green or fuchsin, are immediately decolourised by neutral sulphites. If the test solution is acid, it must be neutralised with sodium bicarbonate. Thiosulphates do not interfere, but sulphides and hydroxides do. Zinc, lead and cadmium salts reduce the sensitivity of the test, hence the interference of sulphides cannot be obviated by the addition of these salts.

Place 1 drop of the dyestuff reagent on a spot plate and add 1 drop of the neutral test solution. The reagent is decolourised.

Sensitivity : 1 μg. SO_2. Concentration limit : 1 in 50,000.

The **malachite green reagent** is prepared by dissolving 0·0025 g. of malachite green in 100 c.c. of water.

† *11.* **Nickelous Hydroxide Test.**—The auto-oxidation of sulphur dioxide (or sulphurous acid) induces the oxidation of green nickelous hydroxide to the black nickelic hydroxide. The colour change is quite distinct, but for very small amounts of sulphur dioxide use may be made of the conversion of benzidine acetate to " benzidine blue " by the higher nickel oxide. Thiosulphates give a similar reaction and must therefore be absent

Place a drop of the test solution (or a little of the test solid) in the tube of the apparatus shown in Fig. 34, and place a little washed nickelous hydroxide on the glass knob under the stopper. Add 1–2 drops of 5–6*N*-hydrochloric acid, close the apparatus and warm gently. The green hydroxide turns grey to black according to the amount of sulphite present. For small amounts of sulphites, transfer the nickel hydroxide to a quantitative filter paper and treat with a drop of the benzidine reagent : a blue colour is formed.

Sensitivity : 0·4 μg. SO_2. Concentration limit : 1 in 125,000.

The **nickelous hydroxide** is prepared by precipitating nickelous chloride solution with sodium hydroxide solution and washing thoroughly until free from alkali. It should be freshly prepared.

The **benzidine reagent** is prepared by dissolving 0·05 g. of benzidine or of its hydrochloride in 10 c.c. of glacial acetic acid, diluting to 100 c.c. with water and filtering.

† *12.* **Sodium Nitroprusside-Zinc Sulphate Test.**—Sodium nitroprusside solution reacts with a solution of a zinc salt to yield a salmon-coloured precipitate of zinc nitroprusside $Zn[Fe(CN)_5NO]$. The latter reacts with moist sulphur dioxide to give a red compound of unknown composition ; the test is rendered more sensitive when the reaction product is held over ammonia vapour which decolourises the unused zinc nitroprusside.

Place a drop of the test solution (or a grain of the solid test sample) in the tube of Fig. 34 and coat the knob of the glass stopper with a thin layer of the zinc nitroprusside paste. Add a drop of 2*N*-hydrochloric or sulphuric acid and close the apparatus. After the sulphur dioxide has been evolved, hold the stopper for a short time in ammonia vapour. The paste is coloured more or less deep red.

Sensitivity : 3·5 μg. SO_2. Concentration limit : 1 in 14,000.

The **zinc nitroprusside paste** is prepared by precipitating sodium nitroprusside solution with an excess of zinc sulphate solution and boiling for a few minutes : the precipitate is filtered and washed, and kept in a dark glass bottle or tube.

The test is not applicable in the presence of sulphides and/or thiosulphates. These can be removed by the addition of mercuric chloride, which reacts forming the acid-stable mercuric sulphide :

$$Hg^{++} + S^{--} = HgS ;$$

$$Hg^{++} + S_2O_3^{--} + H_2O = HgS + SO_4^{--} + 2H^+.$$

Place a drop of the test solution and 2 drops of saturated mercuric chloride solution in the same apparatus (Fig. 34) and, after a minute, acidify with 2*N*-hydrochloric or sulphuric acid, and proceed as above.

20 μg. of Na_2SO_3 can be detected in the presence of 900 μg. of $Na_2S_2O_3$ and 1,500 μg. of Na_2S.

IV, 5. REACTIONS OF THIOSULPHATES, $S_2O_3^{--}$

Solubility.—Most of the thiosulphates that have been prepared are soluble in water ; those of lead, silver and barium are very sparingly soluble. Many of them dissolve in an excess of sodium thiosulphate solution forming complex salts.

Use sodium thiosulphate, $Na_2S_2O_3,5H_2O$.

1. **Dilute Hydrochloric Acid** : no immediate change in the cold with a solution of a thiosulphate ; the acidified liquid soon becomes turbid owing to the separation of sulphur, and sulphurous acid is present in solution. On warming the solution, sulphur dioxide is evolved which is recognised by its odour and its action upon filter paper moistened with acidified potassium dichromate solution. The unstable thiosulphuric acid is first formed ; this soon decomposes largely into sulphurous acid and sulphur. The sulphur first forms a colloidal solution, which is gradually coagulated by the free acid present. Side reactions also occur giving rise to thionic acids.

$$\begin{array}{r} Na_2S_2O_3 + 2HCl = H_2S_2O_3 + 2NaCl\,; \\ H_2S_2O_3 = S + H_2SO_3. \\ \hline Na_2S_2O_3 + 2HCl = SO_2 + H_2O + S + 2NaCl. \end{array}$$

2. **Iodine Solution** : decolourised ; a colourless solution of sodium tetrathionate $Na_2S_4O_6$ is formed.

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

3. **Barium Chloride Solution** : white precipitate of barium thiosulphate BaS_2O_3 from moderately concentrated solutions. Precipitation is accelerated by agitation and by rubbing the sides of the vessel with a glass rod. The solubility is 0·5 g. per litre at 18°. No precipitate is obtained with calcium chloride solution since calcium thiosulphate is fairly soluble in water.

$$Na_2S_2O_3 + BaCl_2 = BaS_2O_3 + 2NaCl.$$

4. **Silver Nitrate Solution** : white precipitate of silver thiosulphate $Ag_2S_2O_3$, readily soluble in excess of the reagent forming the complex salt $Na_3[Ag(S_2O_3)_2]$. The precipitate is unstable, decomposing on standing and rapidly on warming; the colour changes through yellow and brown to black silver sulphide Ag_2S.

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3 + 2NaNO_3\,;$$
$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4\,;$$
$$Ag_2S_2O_3 + 3Na_2S_2O_3 = 2Na_3[Ag(S_2O_3)_2].$$

5. **Lead Acetate Solution** : white precipitate of lead thiosulphate PbS_2O_3, soluble in excess of the precipitant ; on boiling the suspension, a black precipitate containing lead sulphide PbS is obtained (distinction from sulphite).

$$PbS_2O_3 + H_2O = PbS + H_2SO_4.$$

6. **Potassium Cyanide Solution.**—A thiocyanate is produced when a solution of a thiosulphate is boiled with solutions of potassium cyanide and sodium hydroxide. On acidifying with dilute hydrochloric acid and adding ferric chloride solution, the characteristic blood-red colour of ferric thiocyanate is obtained (distinction from sulphite).

$$Na_2S_2O_3 + KCN = KCNS + Na_2SO_3.$$

7. **" Blue Ring " Test.**—When a solution of a thiosulphate mixed with ammonium molybdate solution is poured *slowly* down the side of a test-tube containing concentrated sulphuric acid, a blue ring is formed at the contact zone.

8. **Ferric Chloride Solution**: dark violet colouration (perhaps due to sodium ferri-thiosulphate, $Na[Fe(S_2O_3)_2]$) which disappears after a short time leaving an almost colourless solution.

$$2Na_2S_2O_3 + 2FeCl_3 = Na_2S_4O_6 + 2FeCl_2 + 2NaCl.$$

9. **Nickel Ethylenediamine nitrate Reagent** $[Ni\ en_3]\ (NO_3)_2$.—When a neutral or slightly alkaline solution of a thiosulphate is treated with the reagent, a crystalline violet precipitate of the complex thiosulphate is obtained:

$$[Ni\ en_3](NO_3)_2 + Na_2S_2O_3 = [Ni\ en_3]S_2O_3 + 2NaNO_3.$$

Sulphites, sulphates, tetrathionates and thiocyanates do not interfere, but hydrogen sulphide and ammonium sulphide decompose the reagent with the precipitation of nickel sulphide.

The **nickel ethylenediamine nitrate reagent** is conveniently prepared when required by treating a little nickel nitrate solution with ethylenediamine until a violet colour (due to the formation of the complex $[Ni\ en_3]^{--}$ ion) appears.

The concentration limit is 1 in 25,000.

By obvious modification the reaction may be used for the detection of nickel; it is applicable in the presence of copper, cobalt, iron and chromium.

†*10.* **Catalysis of Iodine-Azide Reaction Test.**—Solutions of sodium azide NaN_3 and of iodine (as KI_3) do not react, but on the addition of a trace of a thiosulphate, which acts as a catalyst, there is an immediate vigorous evolution of nitrogen:

$$2NaN_3 + I_2 = 2NaI + 3N_2.$$

Sulphides and thiocyanates act similarly and must therefore be absent.

Mix a drop of the test solution and a drop of the iodine-azide reagent on a watch glass. A vigorous evolution of bubbles (nitrogen) ensues.

Sensitivity: 0·15 μg. $Na_2S_2O_3$. Concentration limit: 1 in 330,000.

The **sodium azide-iodine reagent** consists of a solution of 1 g. of sodium azide in 100 c.c. of 0·1*N*-iodine.

IV, 6. REACTIONS OF SULPHIDES, S^{--}

Solubility.—The acid, normal and poly-sulphides of the alkali metals are soluble in water; their aqueous solutions react alkaline because of hydrolysis. The normal sulphides of most other metals are insoluble; those of the alkaline earths are difficultly soluble, but are gradually changed by contact with water into soluble hydrosulphides. The sulphides of aluminium, chromium and magnesium are completely hydrolysed by water, and can be prepared only by dry methods. The characteristic colours and solubilities of many metallic sulphides have already been discussed in connexion with the reactions of the cations in Chapter III. The sulphides of iron, manganese, zinc and the alkali metals are decomposed by dilute hydrochloric acid with the evolution of hydrogen sulphide; those of lead, cadmium, nickel, cobalt, antimony and stannic tin require concentrated hydrochloric acid for decomposition; others, such as mercuric sulphide, are insoluble in concentrated hydrochloric acid, but dissolve in aqua regia with the separation of sulphur. The presence of sulphide in insoluble sulphides may be detected by reduction with nascent hydrogen (derived from zinc or tin and hydrochloric acid) to the metal and hydrogen sulphide, the latter being identified with lead acetate paper (see reaction *1* below). An alternative method is to fuse the sulphide with anhydrous sodium carbonate, extract the mass with water and to treat the filtered solution with freshly prepared sodium nitroprusside solution, when a purple colour will be obtained.

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH;$$
$$NaHS + H_2O \rightleftharpoons H_2S + NaOH;$$
$$2CaS + 2H_2O \rightleftharpoons Ca(SH)_2 + Ca(OH)_2;$$
$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Use sodium sulphide, $Na_2S,9H_2O$.

1. **Dilute Hydrochloric Acid***: hydrogen sulphide gas is evolved, which may be identified by its characteristic odour and by the blackening of filter paper moistened with lead acetate solution. A more sensitive test is attained by the use of sodium plumbite solution, prepared by adding sodium hydroxide solution to lead acetate solution until the initial precipitate of lead hydroxide has just dissolved.

$$Na_2S + 2HCl = H_2S + 2NaCl;$$
$$Pb(C_2H_3O_2)_2 + H_2S = PbS + 2H.C_2H_3O_2.$$
$$Pb(ONa)_2 + H_2S = PbS + 2NaOH.$$

Hydrogen sulphide, like sulphur dioxide, is a good reducing agent; it reduces (i) acidified potassium permanganate solution, (ii) acidified potassium dichromate solution and (iii) iodine solution.

$$2KMnO_4 + 5H_2S + 6HCl = 2KCl + 2MnCl_2 + 8H_2O + 5S;$$
$$K_2Cr_2O_7 + 3H_2S + 8HCl = 2KCl + 2CrCl_3 + 7H_2O + 3S;$$
$$H_2S + I_2 \rightleftharpoons 2HI + S.$$

Small quantities of chlorine may be produced in (i) and (ii) if the hydrochloric acid is other than very dilute; this is avoided by using dilute sulphuric acid.

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* Or dilute sulphuric acid.

2. **Silver Nitrate Solution**: black precipitate of silver sulphide Ag_2S, insoluble in cold, but soluble in hot dilute nitric acid.

$$Na_2S + 2AgNO_3 = Ag_2S + 2NaNO_3.$$

3. **Lead Acetate Solution**: black precipitate of lead sulphide PbS (see under Lead, Section **III, 2,** reaction *5*).

4. **Barium Chloride Solution**: no precipitate.

5. **Silver.**—When a solution of a sulphide is brought into contact with a bright silver coin, a brown to black stain of silver sulphide is produced. The result is obtained more expeditiously by the addition of a few drops of dilute hydrochloric acid. The stain may be removed by rubbing the coin with moist lime.

6. **Sodium Nitroprusside Solution** ($Na_2[Fe(CN)_5NO]$): transient purple colour in the presence of solutions of alkalis. No reaction occurs with solutions of hydrogen sulphide or with the free gas: if, however, filter paper is moistened with a solution of the reagent made alkaline with sodium or ammonium hydroxide solution, a purple colouration is produced with free hydrogen sulphide.

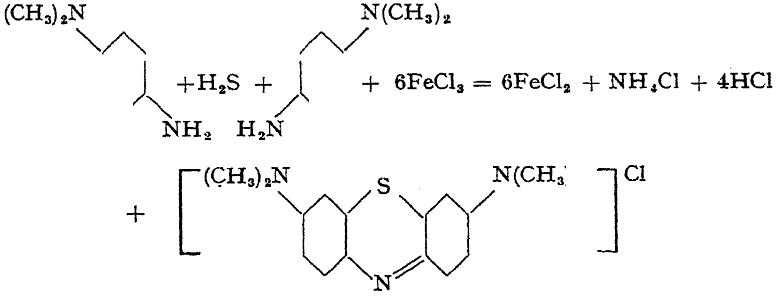
$$Na_2S + Na_2[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS].$$

The *reagent* must be freshly prepared by dissolving a crystal (about the size of a pea) of pure sodium nitroprusside in a little distilled water.

† The spot-test technique is as follows. Mix on a spot plate a drop of the alkaline test solution with a drop of a 1 per cent solution of sodium nitroprusside. A violet colour appears. Alternatively, filter paper impregnated with an ammoniacal (5 per cent) solution of sodium nitroprusside may be employed.

Sensitivity: 1 μg. Na_2S. Concentration limit: 1 in 50,000.

† *7.* **Methylene Blue Test.**—para-Aminodimethylaniline is converted by ferric chloride and hydrogen sulphide in strongly acid solution into the water-soluble dyestuff, methylene blue:



This is a sensitive test for soluble sulphides and hydrogen sulphide.

Place a drop of the test solution on a spot plate, add a drop of concentrated hydrochloric acid, mix, then dissolve a few grains of *p*-aminodimethylaniline in the mixture (or add 1 drop of a 1 per cent solution of the chloride or sulphate) and add a drop of 0·1*N*-ferric chloride solution. A clear blue colouration appears after a short time (2–3 minutes).

Sensitivity: 1 μg. H_2S. Concentration limit: 1 in 50,000.

† *8.* **Catalysis of Iodine-Azide Reaction Test.**—Solutions of sodium azide NaN_3 and of iodine (as KI_3) do not react, but on the addition of a trace of a sulphide, which acts as a catalyst, there is an immediate evolution of nitrogen:

$$2NaN_3 + I_2 = 2NaI + 3N_2.$$

Thiosulphates and thiocyanates act similarly and must therefore be absent. The sulphide can, however, be separated by precipitation with zinc or cadmium carbonate. The precipitated sulphide may then be introduced, say, at the end of a platinum wire into an inverted micro test-tube or centrifuge tube containing the iodine-azide reagent, when the evolution of nitrogen will be seen.

Mix a drop of the test solution and a drop of the reagent on a watch glass. An immediate evolution of gas in the form of fine bubbles occurs.

Sensitivity: 0·3 μg. Na_2S. Concentration limit: 1 in 166,000.

The **sodium azide-iodine reagent** is prepared by dissolving 3 g. of sodium azide in 100 c.c. of 0·1*N*-iodine. The solution is stable. (The test is rendered more sensitive (to 0·02 μg. Na_2S) by employing a more concentrated reagent composed of 1 g. of sodium azide and a few crystals of iodine in 3 c.c. of water.)

IV, 7. REACTIONS OF NITRITES, NO_2^-

Solubility.—Silver nitrite is sparingly soluble in water. All other nitrites are soluble in water.

Use sodium nitrite, $NaNO_2$.

1. **Dilute Hydrochloric Acid.**—Cautious addition of the acid to a solid nitrite in the cold yields a transient, pale-blue liquid (due to the presence of free nitrous acid HNO_2 or its anhydride N_2O_3) and the evolution of brown fumes of nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air. Similar results are obtained with the aqueous solution.

$$NaNO_2 + HCl = HNO_2 + NaCl;$$
$$3HNO_2 = H_2O + HNO_3 + 2NO;$$
$$2NO + O_2 = 2NO_2.$$

2. **Ferrous Sulphate Solution.**—Add the nitrite solution carefully to a concentrated solution of ferrous sulphate acidified with dilute acetic acid or with dilute sulphuric acid;

a brown ring, due to the compound $[Fe,NO]SO_4$, is formed at the junction of the two liquids. If the addition has not been made cautiously, a brown colouration results. This reaction is similar to the brown ring test for nitrates (see Section **IV, 18,** reaction *3*), for which a stronger acid (concentrated sulphuric acid) must be employed.

$$2NaNO_2 + 2H.C_2H_3O_2 = 2Na.C_2H_3O_2 + 2HNO_2\,;$$
$$3HNO_2 = H_2O + HNO_3 + NO\,;$$
$$FeSO_4 + NO = [Fe,NO]SO_4.$$

Iodides, bromides, coloured ions, and anions that give coloured compounds with ferrous salts must be absent.

3. **Barium Chloride Solution** : no precipitate.

4. **Silver Nitrate Solution** : white crystalline precipitate of silver nitrite from concentrated solutions.

$$AgNO_3 + NaNO_2 = AgNO_2 + NaNO_3.$$

5. **Potassium Iodide Solution.**—The addition of a nitrite solution to a solution of potassium iodide, followed by acidification with acetic acid or with dilute sulphuric acid, results in the liberation of iodine, which may be identified by the blue colour produced with starch paste. A similar result is obtained by dipping potassium iodide-starch paper moistened with a little dilute acid into the solution. An alternative method is to extract the liberated iodine with chloroform or carbon tetrachloride (see Section **IV, 16,** reaction *4*).

$$2KI + 2HNO_2 + 2H.C_2H_3O_2 = 2K.C_2H_3O_2 + I_2 + 2NO + 2H_2O.$$

6. **Acidified Potassium Permanganate Solution** : decolourised by a solution of a nitrite, but no gas is evolved.

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

7. **Ammonium Chloride.**—By boiling a solution of a nitrite with excess of the solid reagent, nitrogen is evolved and the nitrite is completely destroyed.

$$NaNO_2 + NH_4Cl = NaCl + N_2 + 2H_2O.$$

8. **Urea** $\{CO(NH_2)_2\}$.—When a solution of a nitrite is treated with urea and the mixture acidified with dilute hydrochloric acid, the nitrite is decomposed, and nitrogen and carbon dioxide are evolved.

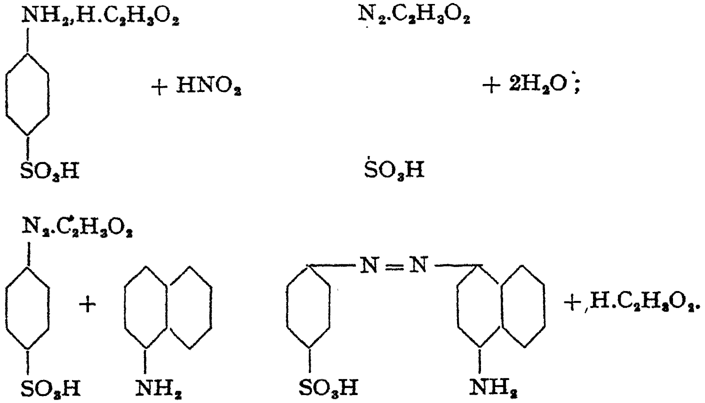
$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O.$$

9. **Thiourea.**—When a dilute acetic acid solution of a nitrite is treated with a little thiourea, nitrogen is evolved and thiocyanic acid is produced. The latter may be identified by the red colour produced with dilute HCl and $FeCl_3$ solution.

$$CS(NH_2)_2 + HNO_2 = N_2 + HCNS + 2H_2O.$$

Thiocyanates and iodides interfere and, if present, must be removed either with excess of solid Ag_2SO_4 or with dilute $AgNO_3$ solution before adding the acetic acid and thiourea.

† 10. **Sulphanilic Acid—α-Naphthylamine Reagent.**—This test depends upon the diazotisation of sulphanilic acid by nitrous acid, followed by coupling with α-naphthylamine to form a red azo dye :



Place a drop of the neutral or acetic acid test solution on a spot plate and mix it with a drop of the sulphanilic acid reagent, followed by a drop of the α-naphthylamine reagent. A red colour is formed.

Sensitivity : 0·01 μg. HNO_2. Concentration limit : 1 in 5,000,000.

The **sulphanilic acid reagent** is prepared by dissolving 1 g. of sulphanilic acid in 100 c.c. of warm 30 per cent acetic acid. The **α-naphthylamine reagent** is prepared by boiling 0·3 g. of α-naphthylamine with 70 c.c. of water, filtering or decanting from the small residue, and mixing with 30 c.c. of glacial acetic acid.

IV, 8. **REACTIONS OF CYANIDES, CN^-

Solubility.—Only the cyanides of the alkali and alkaline earth metals are soluble in water ; the solutions react alkaline owing to hydrolysis. Mercuric cyanide $Hg(CN)_2$ is also soluble in water, but is practically a non-electrolyte and therefore does not exhibit the ionic reactions of cyanides. Many of the metallic cyanides dissolve in solutions of potassium cyanide to yield complex salts (compare Section **I, 20**).

$$KCN + H_2O \rightleftharpoons KOH + HCN.$$

Use potassium cyanide, KCN.

Note. All cyanides are highly poisonous. The free acid HCN is volatile and is particularly dangerous so that all experiments in which the gas is likely to be evolved, or those in which cyanides are heated, should be carried out in the fume cupboard.

1. **Dilute Hydrochloric acid** : hydrocyanic acid HCN, with an odour reminiscent of bitter almonds, is evolved in the cold. It should be smelled with great caution. A more satisfactory method for identifying hydrocyanic acid consists in converting it into ammonium thiocyanate by allowing the vapour to come into contact with a little *yellow* ammonium sulphide on filter paper. The paper may be conveniently placed over the test-tube or dish in which the substance is being treated with the dilute acid. Upon adding a drop of ferric chloride solution and a drop of dilute hydrochloric acid to the filter paper, the characteristic red colouration, due to " ferric thiocyanate," is obtained (see reaction *6* below). Mercuric cyanide is not decomposed by dilute acids.

$$KCN + HCl = KCl + HCN.$$

2. **Silver Nitrate Solution** : white precipitate of silver cyanide AgCN, readily soluble in excess of the reagent forming the complex salt, potassium argentocyanide $K[Ag(CN)_2]$ (compare Section **I, 20**). Silver cyanide is soluble in ammonium hydroxide solution and in sodium thiosulphate solution, but is insoluble in dilute nitric acid.

$$AgNO_3 + KCN = AgCN + KNO_3 ;$$
$$AgCN + KCN = K[Ag(CN)_2].$$

3. **Concentrated Sulphuric Acid.**—Heat a little of the solid salt with concentrated sulphuric acid ; carbon monoxide is evolved which may be ignited and burns with a blue flame. All cyanides, complex and simple, are decomposed by this treatment.

$$2KCN + 2H_2SO_4 + 2H_2O = 2CO + K_2SO_4 + (NH_4)_2SO_4.$$

4. **Prussian Blue Test.**—This is a delicate test and is carried out in the following manner. The solution of the cyanide is rendered strongly alkaline with sodium hydroxide solution, a few c.c. of a freshly prepared solution of ferrous sulphate added (if only traces of cyanide are present, it is best to use a saturated solution of ferrous sulphate) and the mixture boiled. Potassium ferrocyanide is thus formed. Upon acidifying with hydrochloric acid (in order to neutralise any free alkali which may be present), a clear solution is obtained, which gives a precipitate of Prussian blue upon the addition of a little ferric chloride solution. If only a little cyanide was used, or is present, in the solution to be tested, a green solution is obtained at first; this deposits Prussian blue on standing.

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4\,;$$
$$Fe(OH)_2 + 2KCN = Fe(CN)_2 + 2KOH\,;$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]\,;$$
$$3K_4[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

5. **Mercurous Nitrate Solution**: grey precipitate of metallic mercury (difference from choride, bromide and iodide).

$$Hg_2(NO_3)_2 + 2KCN = Hg(CN)_2 + Hg + 2KNO_3.$$

Mercuric cyanide is very little ionised in solution. It is best analyse adding excess of potassium iodide solution when the cyanogen is obtained i ionisable form:

$$Hg(CN)_2 + 4KI = K_2[HgI_4] + 2KCN.$$

Mercuric cyanide is decomposed in solution by hydrogen sulphide, mercuric sulphide (solubility product 4×10^{-53}) being precipitated (compare Solubility Product, Section **I, 15**) and hydrocyanic acid being formed in solution. If the precipitate is filtered off, the thiocyanate test may be applied to the solution.

$$Hg(CN)_2 + H_2S = HgS + 2HCN.$$

6. **"Ferric Thiocyanate" Test.**—This is another excellent test for cyanides and depends upon the direct combination of alkali cyanides with sulphur (best derived from an alkali polysulphide). A little ammonium polysulphide solution is added to the potassium cyanide solution contained in a porcelain dish, and the whole evaporated to dryness on the water bath in the fume cupboard. The residue contains alkali and ammonium thiocyanates together with any residual polysulphide. The latter is destroyed by the addition of a few drops of hydrochloric acid. One or two drops of ferric chloride solution are then added. A blood red colouration, due to ferric ferri-thiocyanate, is immediately produced.

$$KCN + (NH_4)_2S_2 = KCNS + (NH_4)_2S\,;$$
$$6KCNS + 2FeCl_3 \rightleftharpoons Fe[Fe(CNS)_6] + 6KCl$$

† The spot-test technique is as follows. Stir a drop of the test solution with a drop of yellow ammonium sulphide on a watch glass and warm until a rim of sulphur is formed round the liquid (evaporation to dryness, other than on a water bath, should be avoided). Add 1–2 drops of dilute hydrochloric acid, allow to cool, and add 1–2 drops of 3 per cent ferric chloride solution. A red colouration is obtained.

Sensitivity: 1 μg. CN^-. Concentration limit: 1 in 50,000.

The test is applicable in the presence of sulphide or sulphite ; if thiocyanate is originally present, the cyanide must be isolated first by precipitation, *e.g.*, as zinc cyanide.

† *7.* **Copper Sulphide Test.**—Solutions of cyanides readily dissolve cupric sulphide forming the colourless potassium cupri-cyanide :

$$CuS + 4KCN = K_2[Cu(CN)_4] + K_2S.$$

The test is best carried out on filter paper and is applicable in the presence of chlorides, bromides, iodides, ferro- and ferri-cyanides.

Place a drop of a freshly-prepared copper sulphide suspension on a filter paper (or on a spot plate) and add a drop of the test solution. The brown colour of copper sulphides disappears at once.

Sensitivity : 2·5 μg. CN^-. Concentration limit : 1 in 200,000.

The **copper sulphide suspension** is prepared by dissolving 0·12 g. of crystallised copper sulphate in 100 c.c. of water, adding a few drops of ammonia solution, and rendering the solution cloudy with a little hydrogen sulphide.

An *alternative procedure* is to employ quantitative filter paper which has been impregnated with an ammoniacal solution containing 0·1 g. of copper sulphate per 100 c.c. and dried. Immediately before the test a little hydrogen sulphide is blown on to the paper so that it acquires a uniform brown colour. Place a drop of the test solution upon this paper when a white ring will be obtained.

Sensitivity : 2·5 μg. CN^-. Concentration limit : 1 in 20,000.

†*8.* **Copper Acetate-Benzidine Acetate Test.**—This test depends upon the production of nascent oxygen in the intermediate decomposition of cupric cyanide ; the nascent oxygen oxidises the benzidine to a blue quinonoid compound :

$$2Cu(CN)_2 + H_2O = Cu_2(CN)_2 + 2HCN + O.$$

Mix a few drops of the test solution with a little dilute sulphuric acid in a micro test-tube and tie (or otherwise fix) a piece of drop-reaction paper which has been moistened with a mixture of equal parts of the copper acetate and benzidine reagents on to the top of the tube. A blue colouration is produced.

Sensitivity : 0·25 μg. CN^-. Concentration limit : 1 in 200,000.

Oxidising and reducing gases interfere : it has been recommended that the hydrocyanic acid be liberated by heating with sodium bicarbonate.

Alternatively, place a drop of the test solution (or a few milligrams of the test solid) in the reaction bulb of Fig. 37, add 2 thin pieces of zinc and 2–3 drops of dilute sulphuric acid. Place a small piece of quantitative filter paper (or drop-reaction paper) moistened with cupric acetate-benzidine acetate reagent across the funnel. The paper is coloured blue by the hydrocyanic acid carried over with the hydrogen.

Sensitivity : 1 μg. CN^-. Concentration limit : 1 in 50,000.

The **copper acetate reagent** (solution I) is prepared by dissolving 2·86 g. of copper acetate in a litre of water.

The **benzidine reagent** (solution II) consists of 475 c.c. of a solution of benzidine acetate, saturated at room temperature, and 525 c.c. of water.

These solutions are best kept apart in black well-stoppered bottles. Equal volumes of solutions I and II are mixed immediately before required.

IV, 9. **REACTIONS OF CYANATES, CNO^-

Solubility.—The cyanates of the alkalis and of the alkaline earths are soluble in water. Those of silver, mercurous mercury, lead and copper are insoluble in water. The free acid is a colourless liquid with an unpleasant odour; it is very unstable.

Use potassium cyanate, KCNO.

1. **Dilute Sulphuric Acid**: vigorous effervescence, due largely to the evolution of carbon dioxide. The free cyanic acid HCNO, which is initially liberated, is decomposed into carbon dioxide and ammonia, the latter combining with the sulphuric acid present to form ammonium sulphate. A little cyanic acid, however, escapes decomposition and may be recognised in the evolved gas by its penetrating odour. Upon warming the resultant solution with sodium hydroxide solution, ammonia is evolved (test with mercurous nitrate paper).

$$KCNO + H_2SO_4 = HCNO + KHSO_4;$$
$$HCNO + H_2O + H_2SO_4 = CO_2 + NH_4HSO_4.$$

2. **Concentrated Sulphuric Acid.**—The reaction is similar to that with the dilute acid, but is somewhat more vigorous.

3. **Silver Nitrate Solution**: white, curdy precipitate of silver cyanate AgCNO, soluble in ammonium hydroxide solution and in dilute nitric acid (difference from silver cyanide).

$$KCNO + AgNO_3 = AgCNO + KNO_3.$$

4. **Barium Chloride Solution**: no precipitate.

5. **Cobalt Acetate Solution.**—When the reagent is added to a concentrated solution of potassium cyanate, a blue colouration, due to potassium cobaltocyanate $K_2[Co(CNO)_4]$, is produced. The colour is more stable in ethereal solution.

$$Co(C_2H_3O_2)_2 + 4KCNO = K_2[Co(CNO)_4] + 2K.C_2H_3O_2.$$

6. **Copper Sulphate-Pyridine Test.**—When a cyanate is added to a dilute solution of a copper salt to which a few drops of pyridine have been previously added, a lilac blue precipitate is formed of the compound $[Cu(C_5H_5N)_2 (CNO)_2]$; this is soluble in chloroform with the production of a sapphire blue solution. Thiocyanates interfere; excess of copper solution should be avoided.

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† Add a few drops of pyridine to 2–3 drops of a 1 per cent solution of copper sulphate in about 10 c.c. of water, then introduce about 2 c.c. of chloroform followed by a few drops of the neutral cyanate solution.

Shake the mixture briskly : the chloroform will acquire a blue colour.

Concentration limit : 1 part cyanate in 20,000.

The blue complex is stable in the presence of a moderate excess of acetic acid ; the reaction can therefore be applied to the detection of cyanates in alkaline solution. The solution to be tested is added to the copper-pyridine-chloroform mixture, acetic acid added slowly, and the solution shaken vigorously after each addition. As soon as the solution is neutral, the chloroform will assume a blue colour.

IV, 10. **REACTIONS OF THIOCYANATES, CNS^-

Solubility.—Silver and cuprous thiocyanates are practically insoluble in water, mercuric and lead thiocyanates are sparingly soluble ; the solubilities, in g. per litre at 20°, are 0·0003, 0·005, 0·7 and 0·45 respectively. The thiocyanates of the other metals are soluble.

Use potassium thiocyanate (or sulphocyanide), KCNS.

1. **Strong Sulphuric Acid** (*ca.* 14*N*) : decomposition occurs with evolution of carbonyl sulphide, which burns with a blue flame.

$$KCNS + 2H_2SO_4 + H_2O = COS + KHSO_4 + NH_4HSO_4.$$

With *concentrated* H_2SO_4 violent decomposition occurs with the evolution of evil-smelling vapours (largely SO_2) and deposition of S.

2. **Silver Nitrate Solution** : white curdy precipitate of silver thiocyanate AgCNS, soluble in ammonium hydroxide solution, but insoluble in dilute nitric acid.

$$KCNS + AgNO_3 = AgCNS + KNO_3.$$

3. **Copper Sulphate Solution** : solution is coloured green ; with excess of the reagent, black cupric thiocyanate $Cu(CNS)_2$ is precipitated. If a mixture of solutions of cupric sulphate and sulphurous acid be added to the thiocyanate solution, white cuprous thiocyanate $Cu_2(CNS)_2$ is precipitated, insoluble in dilute hydrochloric and sulphuric acids.

$$2KCNS + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$$

4. **Mercuric Nitrate Solution** : white precipitate of mercuric thiocyanate $Hg(CNS)_2$, readily soluble in excess of the thiocyanate solution. If the precipitate is heated, it swells up enormously forming " Pharaoh's serpents," a polymerised cyanogen product.

$$Hg(NO_3)_2 + 2KCNS = Hg(CNS)_2 + 2KNO_3 ;$$

$$Hg(CNS)_2 + 2KCNS = K_2[Hg(CNS)_4].$$

5. **Zinc and Dilute Hydrochloric Acid** : hydrogen sulphide and hydrogen cyanide (*poisonous*) are evolved.

$$KCNS + Zn + 3HCl = H_2S + HCN + ZnCl_2 + KCl.$$

6. **Ferric Chloride Solution** : blood red colouration, due to ferric ferri-thiocyanate $Fe[Fe(CN)_6]$. The latter compound is soluble in ether and hence on shaking with ether the colouration passes into the ethereal layer (compare Section **I, 42**). The colour is discharged by fluorides ($[FeF_6]^{---}$ formed), mercuric chloride ($[Hg(CNS)_4]^{--}$ formed) and oxalates ($[Fe(C_2O_4)_3]^{---}$ formed). Tartrates, other hydroxy organic acids, ferrocyanides, phosphates and also iodides interfere (the last-named because free iodine is produced by ferric ions).

$$6KCNS + 2FeCl_3 = Fe[Fe(CNS)_6] + 6KCl.$$

7. **Cobalt Nitrate Solution** : blue colouration, due to $K_2[Co(CNS)_4]$ (see under Cobalt, Section **III, 24**, reaction *6*), but no precipitate (distinction from cyanide, ferrocyanide and ferricyanide).

† The spot-test technique is as follows. Mix a drop of the test solution in a micro-crucible with a very small drop (0·02 c.c.) of a 1 per cent solution of cobalt sulphate or nitrate and evaporate to dryness. The residue, whether thiocyanate is present or not, is coloured violet and the colour slowly fades. Add a few drops of acetone. A blue-green or green colouration is obtained.

Sensitivity: 1 μg. SCN^-. Concentration limit: 1 in 50,000.

Nitrites yield a red colour due to nitrosyl thiocyanate and therefore interfere with the test.

† *8.* **Catalysis of Iodine-Azide Reaction Test.**—Traces of thiocyanates act as powerful catalysts in the otherwise extremely slow reaction between iodine and sodium azide :

$$I_2 + 2NaN_3 = 2NaI + 3N_2.$$

Sulphides (see Section **IV, 6**, reaction *8*) and thiosulphates (see Section **IV, 5**, reaction *9*) have a similar catalytic effect ; these may be removed by precipitation with mercuric chloride solution :

$$Hg^{++} + S^{--} = HgS ;$$

$$Hg^{++} + S_2O_3^{--} + H_2O = HgS + SO_4^{--} + 2H^+.$$

Considerable amounts of iodine retard the reaction ; iodine is therefore best largely removed by the addition of cold saturated mercuric chloride solution whereupon the complex $[HgI_4]^{--}$ ion, which does not affect the catalysis, is formed.

Mix a drop of the test solution with 1 drop of the iodine-azide reagent on a spot plate. Bubbles of gas (nitrogen) are evolved.

Sensitivity: 1·5 μg. KCNS. Concentration limit: 1 in 30,000.

The **reagent** is prepared by dissolving **3** g. of sodium azide in 100 c.c. of 0·1*N* iodine.

9. **Cupric Sulphate-Pyridine Reagent.**—When a neutral solution of a thiocyanate is added to a dilute solution of a copper salt containing a few drops of pyridine, a yellowish-green precipitate of the composition $[Cu(C_5H_5N)_2(CNS)_2]$ is formed; the compound is soluble in chloroform to which it imparts an emerald green colouration. Cyanates interfere with this reaction; excess of pyridine should be avoided.

† Add a few drops of pyridine to 3–4 drops of a 1 per cent solution of copper sulphate in about 5 c.c. of water, then introduce about 2 c.c. of chloroform, followed by a few drops of the neutral thiocyanate solution. Shake the mixture vigorously. The chloroform will acquire a green colour.

Concentration limit: 1 part thiocyanate in 50,000.

IV, 11.**REACTIONS OF FERROCYANIDES, $[Fe(CN)_6]^{----}$

Solubility.—The ferrocyanides of the alkali and alkaline earth metals are soluble in water; those of the other metals are insoluble in water and in cold dilute acids, but are decomposed by alkalis.

Use potassium ferrocyanide, $K_4[Fe(CN)_6],3H_2O$.

1. **Concentrated Sulphuric Acid**: complete decomposition occurs on warming with the evolution of carbon monoxide, which burns with a blue flame. Hydrogen cyanide is evolved with boiling dilute sulphuric acid.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O = 6CO + FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4.$$

$$2K_4[Fe(CN)_6] + 6H_2SO_4 = K_2Fe[Fe(CN)_6] + 6HCN + 6KHSO_4.$$

2. **Silver Nitrate Solution**: white precipitate of silver ferrocyanide $Ag_4[Fe(CN)_6]$, insoluble in ammonium hydroxide solution (distinction from ferricyanide) and in dilute nitric acid, but soluble in potassium cyanide solution and in sodium thiosulphate solution. Upon warming with concentrated nitric acid, the precipitate is converted into the orange-red silver ferricyanide and is then soluble in ammonia solution.

$$K_4[Fe(CN)_6] + 4AgNO_3 = Ag_4[Fe(CN)_6] + 4KNO_3.$$

3. **Ferric Chloride Solution**: precipitate of Prussian blue $Fe_4[Fe(CN)_6]_3$ in neutral and acid solutions (see under Iron, Section **III, 20,** reaction *5*); the precipitate is decomposed by solutions of caustic alkalis, brown ferric hydroxide being formed.

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4[Fe(CN)_6] + 4Fe(OH)_3.$$

† The spot-test technique is as follows. Mix a drop of the test solution on a spot plate with a drop of ferric chloride solution. A blue precipitate or stain is formed.

Sensitivity: 1·3 µg. $K_4[Fe(CN)_6]$. Concentration limit: 1 in 400,000.

4. **Ferrous Sulphate Solution**: white precipitate of ferrous ferrocyanide $Fe_2[Fe(CN)_6]$, rapidly turning blue owing to oxidation (see under Iron, Section **III, 19**, reaction *6*).

5. **Copper Sulphate Solution**: brown precipitate of copper ferrocyanide $Cu_2[Fe(CN)_6]$, insoluble in dilute acetic acid, but decomposed by solutions of caustic alkalis.

$$K_4[Fe(CN)_6] + 2CuSO_4 = Cu_2[Fe(CN)_6] + 2K_2SO_4.$$

6. **Thorium Nitrate Solution**: white precipitate of thorium ferrocyanide $Th[Fe(CN)_6]$, which is difficult to filter (distinction and separation from ferricyanide and thiocyanate).

$$Th(NO_3)_4 + K_4[Fe(CN)_6] = 4KNO_3 + Th[Fe(CN)_6].$$

7. **Hydrochloric Acid.**—Treatment of a concentrated solution of potassium ferrocyanide with hydrochloric acid results in the formation of hydroferrocyanic acid $H_4[Fe(CN)_6]$, which may be isolated by extraction with ether, and obtained as a white solid.

$$K_4[Fe(CN)_6] + 4HCl = 4KCl + H_4[Fe(CN)_6].$$

8. **Ammonium Molybdate in Dilute Hydrochloric Acid Solution**: brown precipitate of molybdenyl ferrocyanide (difference and separation from ferricyanide and thiocyanate), insoluble in dilute acids but soluble in solutions of alkali hydroxides.

9. **Dilute Sulphuric Acid.**—No reaction takes place in the cold, but on boiling partial decomposition occurs with the formation of ferrous iron and the evolution of hydrocyanic acid. The former reacts with the unchanged ferrocyanide yielding ultimately Prussian blue (see under Iron, Section **III, 19,** reaction *6*).

$$K_4[Fe(CN)_6] + 3H_2SO_4 \rightleftharpoons 6HCN + FeSO_4 + 2K_2SO_4.$$

10. **Cobalt Nitrate Solution**: greyish-green precipitate of cobalt ferrocyanide $Co_2[Fe(CN)_6]$ with excess of the reagent, insoluble in dilute hydrochloric and dilute acetic acids.

† *11.* **Uranyl Acetate Solution**: brown precipitate of uranyl ferrocyanide $(UO_2)_2[Fe(CN)_6]$ in the presence of dilute acetic acid. Ferricyanides react only in concentrated solutions, and after long standing or heating to give the dirty yellow uranyl ferricyanide. Ferricyanides are

reduced by filter paper to ferrocyanides, hence the test should not be carried out on filter paper.

Place a drop of the test solution on a spot plate and add a drop of *N*-uranyl acetate solution. A brown precipitate or spot is obtained within 2 minutes.

Sensitivity: 1 μg. $K_4[Fe(CN)_6]$. Concentration limit: 1 in 50,000.

12. **Action of Heat.**—All ferrocyanides are decomposed on heating, nitrogen and cyanogen being evolved.

$$3K_4[Fe(CN)_6] = N_2 + 2(CN)_2 + 12KCN + Fe_3C + C.$$

IV, 12. **REACTIONS OF FERRICYANIDES, $[Fe(CN)_6]^{---}$

Solubility.—The ferricyanides of the alkali and alkaline earth metals and of ferric iron are soluble in water; those of most of the other metals are insoluble or sparingly soluble.

Use potassium ferricyanide, $K_3[Fe(CN)_6]$.

1. **Concentrated Sulphuric Acid.**—On warming a solid ferricyanide with this acid, it is completely decomposed, carbon monoxide being evolved.

$$2K_3[Fe(CN)_6] + 12H_2SO_4 + 12H_2O$$
$$= 12CO + Fe_2(SO_4)_3 + 3K_2SO_4 + 6(NH_4)_2SO_4.$$

With dilute sulphuric acid, no reaction occurs in the cold but on boiling hydrocyanic acid is evolved.

2. **Silver Nitrate Solution**: orange-red precipitate of silver ferricyanide $Ag_3[Fe(CN)_6]$, soluble in ammonium hydroxide solution (distinction from ferrocyanide), but insoluble in dilute nitric acid.

$$K_3[Fe(CN)_6] + 3AgNO_3 = Ag_3[Fe(CN)_6] + 3KNO_3.$$

3. **Ferrous Sulphate Solution**: dark blue precipitate (Turnbull's blue) of ferrous ferricyanide $Fe_3[Fe(CN)_6]_2$ in neutral and acid solutions, insoluble in oxalic acid solution (see under Iron, Section **III, 19,** reaction *7*). The precipitate is decomposed by solutions of caustic alkalis with the formation of ferrous hydroxide and alkali ferricyanide.

$$Fe_3[Fe(CN)_6]_2 + 6NaOH = 2Na_3[Fe(CN)_6] + 3Fe(OH)_2.$$

4. **Ferric Chloride Solution**: brown colouration, due to ferric ferricyanide $Fe[Fe(CN)_6]$ (see Iron, Section **III, 20,** reaction *6*) or possibly to ferric cyanide $Fe(CN)_3$.

$$K_3[Fe(CN)_6] + FeCl_3 \rightleftharpoons 2Fe(CN)_3 + 3KCl.$$

5. **Copper Sulphate Solution**: green precipitate of cupric ferricyanide $Cu_3[Fe(CN)_6]_2$, insoluble in hydrochloric acid.

$$2K_3[Fe(CN)_6] + 3CuSO_4 = Cu_3[Fe(CN)_6]_2 + 3K_2SO_4.$$

6. **Concentrated Hydrochloric Acid.**—The addition of concentrated hydrochloric acid to a cold saturated solution of potassium ferricyanide results in the separation of brown ferricyanic acid $H_3[Fe(CN)_6]$.

7. **Potassium Iodide Solution** : iodine is liberated, which may be identified by the blue colour produced with starch solution.

$$2K_3[Fe(CN)_6] + 2KI = 2K_4[Fe(CN)_6] + I_2.$$

8. **Cobalt Nitrate Solution** : red precipitate of cobalt ferricyanide $Co_3[Fe(CN)_6]_2$, insoluble in hydrochloric acid but soluble in ammonia solution.

† *9.* **Benzidine Reagent** : blue precipitate of oxidation product. Other oxidising agents (molybdates, chromates, etc.) must be absent. The test is applicable in the presence of ferrocyanide for benzidine ferrocyanide is white : the sensitivity is, however, reduced and it is best to precipitate the ferrocyanide first as the white insoluble lead ferrocyanide by the addition of lead acetate, the ferricyanide remaining in solution.

Mix a drop of the test solution on a spot plate with a drop of the benzidine reagent. If ferrocyanides are present, a drop of 1 per cent lead nitrate solution should be added before the reagent. A blue precipitate or colouration appears.

Sensitivity : 1 μg. $K_3[Fe(CN)_6]$. Concentration limit : 1 in 50,000.
The **reagent** consists of $2N$-acetic acid saturated with benzidine.

10. **Action of Heat.**—The decomposition is similar to that of ferrocyanides (Section **IV, 11**, reaction *12*).

$$6K_3[Fe(CN)_6] = 6N_2 + 3(CN)_2 + 18KCN + 2Fe_3C + 10C.$$

IV, 13. **REACTION OF HYPOCHLORITES, ClO^-

Solubility.—All hypochlorites are soluble in water. The solutions are alkaline because of hydrolysis, and are decomposed by boiling.

$$NaOCl + H_2O \rightleftharpoons HOCl + NaOH.$$

Use a solution of sodium hypochlorite, NaOCl.*

1. **Dilute Hydrochloric Acid** : the solution at first assumes a yellow colour, effervescence occurs and chlorine is evolved. The gas may be identified (*a*) by its greenish-yellow colour and irritating odour, (*b*) by its bleaching of litmus paper, and (*c*) by its action upon potassium iodide-starch paper which it turns blue-black.

$$NaOCl + HCl = HOCl + NaCl;$$
$$HOCl + HCl = Cl_2 + H_2O.$$

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* Chloride is invariably present, and this will vitiate many ionic reactions.

2. **Potassium Iodide-Starch Paper** : assumes a bluish-black colour in weakly alkaline solution as a result of the separation of iodine.

$$2KI + NaOCl + H_2O = I_2 + 2KOH + NaCl.$$

3. **Lead Acetate or Lead Nitrate Solution** : brown lead dioxide PbO_2 is produced on boiling.

$$Pb(C_2H_3O_2)_2 + NaOCl + H_2O = 2H.C_2H_3O_2 + PbO_2 + NaCl.$$

4. **Cobalt Nitrate Solution.**—Add a few drops of the reagent to a solution of the hypochlorite ; a black precipitate of cobalt oxide is obtained. On warming, oxygen is evolved (identified by the rekindling of a glowing splint), the cobalt oxide acting as a catalyst.

5. **Mercury.**—On shaking a slightly acidified (sulphuric acid) solution of a hypochlorite with mercury, a brown precipitate of basic mercuric chloride $(HgCl)_2O$ is formed, which is insoluble in water, but soluble in dilute hydrochloric acid. The precipitate is filtered off and dissolved in dilute hydrochloric acid ; a black precipitate of mercuric sulphide is obtained on passing hydrogen sulphide into the solution.

Chlorine water, under similar conditions, gives a white precipitate of mercurous chloride Hg_2Cl_2, insoluble in hydrochloric acid.

$$2Hg + 2HOCl = (HgCl)_2O + 2HCl ;$$
$$(HgCl)_2O + 2HCl = 2HgCl_2 + H_2O.$$

IV, 14. 96. REACTIONS OF CHLORIDES, Cl^-

Solubility.—Most chlorides are soluble in water. Mercurous chloride Hg_2Cl_2, silver chloride AgCl, lead chloride $PbCl_2$ (this is sparingly soluble in cold but readily soluble in boiling water), cuprous chloride Cu_2Cl_2, bismuth oxychloride BiOCl, antimony oxychloride SbOCl and mercuric oxychloride Hg_2OCl_2 are insoluble in water.

Use sodium chloride, NaCl.

1. **Concentrated Sulphuric Acid** : considerable decomposition of the chloride occurs in the cold, completely on warming, with the evolution of hydrogen chloride, which is recognised (*a*) by its pungent odour and the production of white fumes, consisting of fine drops of hydrochloric acid, on blowing across the mouth of the tube, (*b*) by the formation of white clouds of ammonium chloride when a glass rod moistened with ammonium hydroxide solution is held near the mouth of the vessel, and (*c*) by its turning blue litmus paper red.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

2. **Manganese Dioxide and Concentrated Sulphuric Acid.**—If the solid chloride is mixed with an equal quantity of precipitated manganese dioxide*, concentrated sulphuric acid added and the mixture gently warmed, chlorine is evolved which is identified by its suffocating odour, yellowish-green colour, its bleaching of moistened litmus paper, and turning of potassium iodide-starch paper blue. The hydrogen chloride first formed is oxidised to chlorine.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

3. **Silver Nitrate Solution**: white, curdy precipitate of silver chloride AgCl, insoluble in water and in dilute nitric acid, but soluble in *dilute* ammonium hydroxide solution and in potassium cyanide and sodium thiosulphate solutions (see under Silver, Section **III, 4,** reaction *1*; also Complex Ions Section **I, 20**). The silver chloride is re-precipitated from the ammoniacal solution by the addition of dilute nitric acid.

$$NaCl + AgNO_3 = AgCl + NaNO_3;$$
$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl;$$
$$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl + 2NH_4NO_3.$$

If the silver chloride precipitate is filtered off, washed with distilled water, and then shaken with sodium arsenite solution it is converted into yellow silver arsenite and sodium chloride is formed (distinction from silver bromide and silver iodide, which are unaffected by this treatment). This may be used as a confirmatory test for a chloride.

$$Na_3AsO_3 + 3AgCl = 3NaCl + Ag_3AsO_3.$$

4. **Lead Acetate Solution**: white precipitate of lead chloride $PbCl_2$ from concentrated solutions (see under Lead, Section **III, 2,** reaction *1*).

5. **Potassium Dichromate and Sulphuric Acid (Chromyl Chloride Test).**—The solid chloride is intimately mixed with three times its weight of powdered potassium dichromate in a small distilling flask (Fig. 43), an equal bulk of concentrated sulphuric acid added and the mixture gently warmed‡. The deep-red vapours of chromyl chloride CrO_2Cl_2 which are evolved are passed into sodium hydroxide solution contained in a test-tube. The resultant yellow solution in the test-tube contains sodium chromate; this is confirmed by acidifying with dilute sulphuric acid, adding 2–3 c.c. of ether (*highly*

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* The commercial substance (pyrolusite) usually contains considerable quantities of chlorides.

‡ This test must not be carried out in the presence of chlorates because of the danger of forming explosive chlorine dioxide (Section **IV, 19**, reaction *1*).

inflammable) followed by a little hydrogen peroxide. The ethereal solution is coloured blue. Alternatively, the diphenylcarbazide reagent test (Section **IV, 33,** reaction *10*) may be applied. The formation of a chromate in the distillate indicates that a chloride was present in the solid substance, since chromyl chloride is a readily volatile chromium compound. Bromides and chlorides give rise to the free halogens, which yield colourless solutions with sodium hydroxide solution, and hence this test may be employed for the identification of chlorides in the presence of bromides and iodides. Fluorides must, however, be absent for they give rise to the volatile liquid chromyl fluoride CrO_2F_2, which is decomposed by water.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O\,;$$

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O.$$

The chlorides of mercury, owing to their slight ionisation, do not respond to this test. Only partial conversion to CrO_2Cl_2 occurs with the chlorides of lead, silver, antimony and tin.

† The spot-test technique is as follows. Into the tube of Fig. 38 place a few milligrams of the solid sample (or evaporate a drop or two of the test solution in it), add a small quantity of powdered potassium dichromate and a drop of concentrated sulphuric acid. Place a column about 1 mm. long of a 1 per cent solution alcoholic diphenylcarbazide solution into the capillary of the stopper and heat the apparatus for a few minutes. The chromyl chloride evolved causes the reagent to assume a violet colour.

Sensitivity: 1·5 μg. Cl^-. Concentration limit: 1 in 30,000.

Alternatively, employ the same quantities of materials in the apparatus of Fig. 34, and replace the diphenylcarbazide solution by a drop of dilute alkali on the glass knob. Warm for a few minutes and, after cooling, dip the glass knob into a few drops of the alcoholic diphenylcarbazide solution which has been treated with a little dilute sulphuric acid and is contained on a spot plate. A violet colouration is obtained.

Sensitivity: 0·3 μg. Cl^-. Concentration limit: 1 in 150,000.

Small amounts of bromides and iodides do not interfere, but large amounts of bromides give rise to sufficient bromine to oxidise the reagent. It is therefore best to add a little phenol to the reagent solution, whereupon the bromine is removed as tribromophenol. Nitrates interfere since nitrosyl chloride is formed, but they may be reduced to ammonium salts.

IV, 15. REACTIONS OF BROMIDES, Br^-

Solubility.—Silver, mercurous and cuprous bromides are insoluble in water. Lead bromide is sparingly soluble in cold, but more soluble in boiling water. All other bromides are soluble.

Use potassium bromide, KBr.

1. **Concentrated Sulphuric Acid.**—With the solid bromide, a reddish-brown solution is first formed and reddish-brown vapours of bromine accompany the hydrogen bromide (fuming in moist air) which is evolved ; the reaction is accelerated by warming. The bromine is produced by the oxidation of the hydrogen bromide by the sulphuric acid. If syrupy phosphoric acid H_3PO_4 is substituted for the sulphuric acid and the mixture warmed, only hydrogen bromide, the properties of which are similar to hydrogen chloride, is evolved.

$$KBr + H_2SO_4 = KHSO_4 + HBr;$$
$$2HBr + H_2SO_4 \rightleftharpoons Br_2 + SO_2 + 2H_2O.$$
$$KBr + H_3PO_4 = KH_2PO_4 + HBr.$$

2. **Manganese Dioxide and Concentrated Sulphuric Acid.**—When a mixture of a solid bromide, precipitated manganese dioxide and concentrated sulphuric acid is warmed, reddish-brown vapours of bromine are evolved, which is recognised (*a*) by its powerful irritating odour, (*b*) by its bleaching of litmus paper, and (*c*) by its staining of starch paper orange-red.

$$2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 3H_2O.$$

3. **Silver Nitrate Solution** : curdy, pale-yellow precipitate of silver bromide AgBr, sparingly soluble in dilute, but readily soluble in concentrated ammonium hydroxide solution. The precipitate is also soluble in potassium cyanide and sodium thiosulphate solutions, but insoluble in dilute nitric acid.

$$AgBr + 2NH_3 = [Ag(NH_3)_2]Br;$$
$$AgBr + 2KCN = [Ag(CN)_2]K + KBr.$$

4. **Lead Acetate Solution** : white crystalline precipitate of lead bromide $PbBr_2$, sparingly soluble in cold, but soluble in boiling water.

$$2KBr + Pb(C_2H_3O_2)_2 = PbBr_2 + 2K.C_2H_3O_2.$$

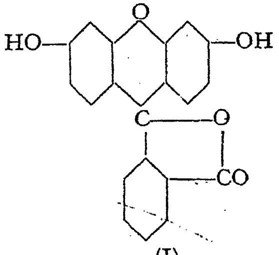
5. **Chlorine Water.**—The addition of this reagent drop-wise to a solution of a bromide liberates free bromine, which colours the solution orange-red ; if carbon disulphide, chloroform or carbon tetrachloride (2 c.c.) is added and the liquid shaken, the bromine dissolves in the solvent (see The Distribution Law, Section **I, 42**) and, after allowing to stand, forms a reddish-brown solution below the colourless aqueous layer. With excess of chlorine water, the bromine is converted into yellow bromine monochloride or into colourless hypobromous or bromic acid, and a pale-yellow or colourless solution results (difference from iodide).

$$2KBr + Cl_2 = 2KCl + Br_2\,;$$
$$Cl_2 + Br_2 + 2H_2O = 2HOBr + 2HCl\,;$$
$$5Cl_2 + Br_2 + 6H_2O = 2HBrO_3 + 10HCl.$$

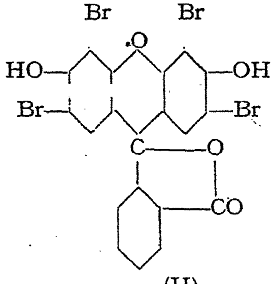
6. **Potassium Dichromate and Concentrated Sulphuric Acid.**—On gently warming a mixture of a solid bromide, concentrated sulphuric acid and potassium dichromate (see Chlorides, Section **IV, 14,** reaction *5*) and passing the evolved vapours into water, a yellowish-brown solution, containing free bromine but no chromium, is produced. A colourless (or sometimes a pale yellow) solution is obtained on treatment with sodium hydroxide solution; this does not give the chromate reaction with dilute sulphuric acid, hydrogen peroxide and ether, or with the diphenylcarbazide reagent (distinction from chloride).

$$K_2Cr_2O_7 + 6KBr + 7H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O.$$

† *7.* **Fluorescein Test.**—Free bromine converts the yellow dyestuff fluorescein (I) into the red tetrabromo-fluorescein or eosin (II). Filter paper impregnated with fluorescein solution is therefore a valuable reagent for bromine vapour since it becomes red.



(I)



(II)

Chlorine tends to bleach the reagent. Iodine forms the red-violet coloured iodo-eosin and hence must be absent. If the bromide is oxidised to free bromine by heating with lead dioxide and acetic acid, practically no chlorine is simultaneously evolved from chlorides, and hence the test may be conducted in the presence of chlorides.

$$2NaBr + PbO_2 + 4H.C_2H_3O_2 = Pb(C_2H_3O_2)_2 + 2K.C_2H_3O_2 + Br_2 + 2H_2O.$$

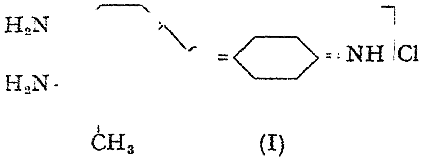
Place a drop of the test solution together with a few milligrams of lead dioxide and acetic acid into the apparatus of Fig. 37, and close the tube with the funnel stopper carrying a piece of filter paper which has been impregnated with the reagent and dried. Warm the apparatus gently. A circular red spot is formed on the yellow test paper.

Alternatively, the apparatus of Fig. 38 may be used; a column, about 1 mm. long of the reagent, is employed.

Sensitivity: 2 μg. Br_2. Concentration limit: 1 in 25,000.

The **fluorescein reagent** consists of a saturated solution of fluorescein in 50 per cent alcohol.

† *8.* **Fuchsin (or Magenta) Test.**—The dyestuff fuchsin (I) forms a



(I)

colourless addition compound with a bisulphite. Free bromine converts the thus-decolourised fuchsin into a blue or violet brominated dyestuff. Neither free chlorine nor free iodine affect the colourless fuchsin bisulphite compound, hence the reaction may be employed for the detection of bromides in the presence of chlorides and iodides.

Place a drop of the test solution (or a few milligrams of the test solid) in the tube of the apparatus shown in Fig. 38, add 2–4 drops of 25 per cent chromic acid solution, and close the apparatus with the "head" which contains 1–2 drops of the reagent solution in the capillary. Warm the apparatus gently (do not allow it to boil). In a short time the liquid in the capillary assumes a violet colour.

Sensitivity: 3 μg. Br^-. Concentration limit: 1 in 15,000.

The **fuchsin-bisulphite reagent** consists of a 0·1 per cent fuchsin solution just decolourised by sodium bisulphite.

IV, 16. REACTION OF IODIDES, I^-

Solubility.—The solubilities of the iodides are similar to those of the chlorides and bromides. Silver, mercurous, mercuric, cuprous and lead iodides are the least soluble salts.

Use potassium iodide, KI.

1. **Concentrated Sulphuric Acid.**—With a solid iodide, iodine is liberated; on warming, violet vapours are evolved, which turn starch paper blue. Some hydrogen iodide is formed—this can be seen by blowing across the mouth of the vessel, when white fumes are produced—but most of it reduces the sulphuric acid to sulphur dioxide, hydrogen sulphide and sulphur, the relative proportions of which depend upon the concentrations of the reagents. Pure hydrogen iodide is formed on warming with syrupy phosphoric acid.

$$KI + H_2SO_4 = KHSO_4 + HI\,;$$
$$H_2SO_4 + 2HI \rightleftharpoons I_2 + SO_2 + 2H_2O\,;$$
$$H_2SO_4 + 6HI = 3I_2 + S + 4H_2O\,;$$
$$H_2SO_4 + 8HI = 4I_2 + H_2S + 4H_2O.$$
$$KI + H_3PO_4 = KH_2PO_4 + HI.$$

If manganese dioxide is added to the mixture, only iodine is evolved.

$$2KI + MnO_2 + 3H_2SO_4 = I_2 + 2KHSO_4 + MnSO_4 + \underset{2}{3}H_2O.$$

2. **Silver Nitrate Solution**: yellow, curdy precipitate of silver iodide AgI, readily soluble in potassium cyanide and in sodium thiosulphate solutions, very slightly soluble in concentrated ammonium hydroxide solution, and insoluble in dilute nitric acid.

$$KI + AgNO_3 = AgI + KNO_3.$$

3. **Lead Acetate Solution**: yellow precipitate of lead iodide PbI_2, soluble in much hot water forming a colourless solution, and yielding golden-yellow plates (" spangles ") on cooling.

$$Pb(C_2H_3O_2)_2 + 2KI = PbI_2 + 2K.C_2H_3O_2.$$

4. **Chlorine Water.**—When this reagent is added drop-wise to a solution of an iodide, iodine is liberated, which colours the solution brown; on shaking with 1–2 c.c. of carbon disulphide, chloroform or carbon tetrachloride (see Section **I, 42**), it dissolves forming a violet solution, which settles out below the aqueous layer. The free iodine may also be identified by the characteristic blue colour it forms with starch solution. If excess of chlorine water is added, the iodine is oxidised to colourless iodic acid.

$$2KI + Cl_2 = 2KCl + I_2\,;$$
$$5Cl_2 + I_2 + 6H_2O = 2HIO_3 + 10HCl.$$

5. **Potassium Dichromate and Concentrated Sulphuric Acid**: only iodine is liberated, and no chromate is present in the distillate (see Chlorides, Section **IV, 14**, reaction *5*) (difference from chloride).

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4$$
$$= 3I_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O.$$

6. **Sodium Nitrite Solution.**—Iodine is liberated when this reagent is added to an iodide solution acidified with dilute acetic or sulphuric acid (difference from bromide and chloride).

The iodine may be identified by colouring starch paste blue, or carbon tetrachloride violet.

$$NaNO_2 + H.C_2H_3O_2 = HNO_2 + Na.C_2H_3O_2;$$
$$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O.$$

7. **Copper Sulphate Solution**: brown precipitate consisting of a mixture of cuprous iodide Cu_2I_2 and iodine. The iodine may be removed by the addition of sodium thiosulphate solution or sulphurous acid, and a nearly white precipitate of cuprous iodide obtained.

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

8. **Mercuric Chloride Solution**: scarlet precipitate of mercuric iodide HgI_2, soluble in excess of potassium iodide solution.

$$HgCl_2 + 2KI = HgI_2 + 2KCl;$$
$$HgI_2 + 2KI = K_2[HgI_4].$$

† *9.* **Starch Test.**—Iodides are readily oxidised in acid solution to free iodine by a number of oxidising agents; the free iodine may then be identified by the deep blue colouration produced with starch solution. The best oxidising agent to employ in the spot-test reaction is acidified potassium nitrite solution:

$$2HI + 2HNO_2 = I_2 + 2NO + 2H_2O.$$

Cyanides interfere because of the formation of cyanogen iodide; they are therefore removed before the test by acidifying and heating:

$$I_2 + HCN \rightleftharpoons ICN + HI.$$

Mix a drop of the acid test solution on a spot plate with a drop of the reagent and add a drop of 10 per cent potassium nitrite solution. A blue colouration is obtained.

Sensitivity: 2·5 μg. I_2. Concentration limit: 1 in 20,000.

The **starch reagent** is prepared by mixing 1 g. of soluble starch and 0·005 g. of mercuric iodide (which acts as a preservative) with a little water into a paste and then pouring 500 c.c. of boiling water over the paste.

† *10.* **Catalytic Reduction of Ceric Salts Test.**—The reduction of ceric salts in acid solution by arsenites takes place very slowly:

$$2Ce^{++++} + AsO_3^{---} + H_2O = 2Ce^{+++} + AsO_4^{---} + 2H^+.$$

Iodides accelerate this change, possibly owing to iodine liberated in the instantaneous reaction (i):

$$2Ce^{++++} + 2I^- = 2Ce^{+++} + I_2 \qquad \text{(i)},$$

reacting according to (ii):

$$AsO_3^{---} + I_2 + H_2O = AsO_4^{---} + 2I^- + 2H^+ \qquad \text{(ii)},$$

the iodide ion reacting again as in (i). The completion of the reduction is indicated by the disappearance of the yellow colour of the ceric solution. Osmium and ruthenium salts have a similar catalytic effect. Moderate amounts of chlorides, bromides, sulphates and nitrates have no influence, but cyanides, mercuric, silver and manganese salts interfere.

Place a drop of the test solution together with a drop each of neutral or slightly acid $0{\cdot}1N$-sodium arsenite solution and $0{\cdot}05N$-ceric ammonium sulphate solution (in $2N$-sulphuric acid) on a spot plate. The yellow colour soon disappears.

Sensitivity: 0·03 μg. I^-. Concentration limit: 1 in 1,000,000.

† *11.* **Palladous Chloride Test.**—Solutions of iodides react with palladous chloride solution to yield a brownish-red precipitate of palladous iodide PdI_2, insoluble in mineral acids.

Mix a drop of the test solution on drop reaction paper with a drop of a 1 per cent aqueous solution of palladous chloride. A brownish-black precipitate forms.

Sensitivity: 1 μg. I^-. Concentration limit: 1 in 50,000.

IV, 17. REACTIONS OF FLUORIDES, F^-

Solubility.—The fluorides of the common alkali metals and of silver, mercury, aluminium and nickel are readily soluble in water, those of lead, copper, ferric iron, barium and lithium are slightly soluble, and those of the alkaline earth metals are insoluble in water.

Use sodium fluoride, NaF.

1. **Concentrated Sulphuric Acid.**—With the solid fluoride, a colourless, corrosive gas, hydrogen fluoride HF, is evolved on warming; the gas fumes in moist air, and the test-tube acquires a greasy appearance as a result of the corrosive action of the vapour on the silica in the glass, which liberates the gas, silicon tetrafluoride SiF_4. By holding a moistened glass rod in the vapour, gelatinous silicic acid H_4SiO_4 is deposited on the rod; this is a product of the decomposition of the silicon tetrafluoride.

$$NaF + H_2SO_4 = NaHSO_4 + HF;$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O;$$

$$3SiF_4 + 4H_2O = 2H_2[SiF_6] + H_4SiO_4.$$

The same result is more readily attained by mixing the solid fluoride with an equal bulk of silica, making into a paste with concentrated sulphuric acid and warming gently; silicon tetrafluoride is readily evolved.

† The spot-test technique of the reaction utilises the conversion of the silicic and fluosilicic acids by means of ammonium molybdate into silico-molybdic acid $H_4[SiMo_{12}O_{40}]$. The latter, unlike free molybdic acid, oxidises benzidine in acetic acid solution to a blue dyestuff and "molybdenum blue" is simultaneously produced.

Mix the solid test sample with a little pure silica in the tube of the apparatus shown in Fig. 34 and moisten the silica with 1–2 drops of concentrated sulphuric acid. Place a drop of water on the glass knob of the stopper, insert it in position, and heat the apparatus gently for about 1 minute. Remove the source of heat and allow to stand for 5 minutes. Wash the drop of water into a micro-crucible, add 1–2 drops of the ammonium molybdate reagent and warm the mixture until bubbling just commences. Allow to cool, introduce a drop of a 1 per cent solution of benzidine in 10 per cent acetic acid and a few drops of saturated sodium acetate solution. A blue colour is obtained.

Sensitivity: 1 μg. F.

The **ammonium molybdate reagent** is prepared by dissolving 1·5 g. of ammonium molybdate in 30 c.c. of water and pouring into 10 c.c. of nitric acid (sp. gr. 1·2).

2. **The Etching Test.**—A clean watch-glass is coated on the convex side with paraffin wax, and part of the glass is exposed by scratching a design on the wax with a nail or wire. A mixture of about 0·5 g. of the fluoride and 2 c.c. of concentrated sulphuric acid is placed in a small lead or platinum crucible, and the latter immediately covered with the watch-glass, convex side down. A little water should be poured in the upper (concave) side of the watch-glass to prevent the wax from melting. The crucible is very gently warmed (best on a boiling water bath). After 5–10 minutes, the hydrogen fluoride will have etched the glass. This is readily seen on removing the paraffin wax by holding above a flame or with hot water, and breathing upon the surface of the glass.

Silicates and borates interfere and should therefore be absent.

3. **Silver Nitrate Solution**: no precipitate, since silver fluoride is soluble in water.

4. **Calcium Chloride Solution**: white, slimy precipitate of calcium fluoride CaF_2, insoluble in acetic acid, but slightly soluble in dilute hydrochloric acid.

$$2NaF + CaCl_2 = CaF_2 + 2NaF.$$

5. **Ferric Chloride Solution**: white crystalline precipitate of the complex salt $Na_3[FeF_6]$ from concentrated solutions of fluorides, sparingly soluble in water. The precipitate does not give the reactions of iron (*e.g.*, with ammonium thiocyanate), except upon acidification.

$$FeCl_3 + 6NaF = Na_3[FeF_6] + 3NaCl.$$

†6. **Zirconium-Alizarin Lake Test.**—Hydrochloric acid solutions of zirconium salts are coloured reddish-violet by alizarin-S or by alizarin (see under Aluminium, Section **III, 21**, reactions *8* and *9*, and under Zirconium, Section **VII, 17**, reactions *11* and *12*); upon adding a solution

of a fluoride the colour of such solutions changes immediately to a pale yellow (that of the liberated alizarin sulphonic acid or alizarin) because of the formation of the colourless zirconi-fluoride ion $[ZrF_6]^{--}$. The test may be performed on a spot plate.

Mix together on a spot plate 2 drops each (equal volumes) of a 0·1 per cent aqueous solution of alizarin-S (sodium alizarin sulphonate) and a 0·1 per cent solution of zirconium nitrate in 20 per cent hydrochloric acid: upon the addition of a drop or two of the fluoride solution the zirconium lake is decolourised to a clear yellow solution.

The most sensitive method of carrying out the spot-test is as follows. Impregnate some quantitative filter paper with the zirconium-alizarin reagent, dry it and moisten with a drop of 50 per cent acetic acid. Place a drop of the neutral test solution upon the moist red spot; the spot will turn yellow. With small amount of fluoride, it is best to heat the paper in steam.

Sensitivity: 1 μg. F^-. Concentration limit: 1 in 50,000.

Large amounts of sulphates, thiosulphates, arsenates, phosphates and oxalates interfere with the test.

The **zirconium-alizarin reagent** is prepared as follows. Heat zirconium dioxide with dilute hydrochloric acid and filter; the solution should contain about 0·0005 g. of Zr per c.c. Treat several c.c. of the zirconium solution with a slight excess of an alcoholic solution of alizarin; excess of alizarin is detected by extracting a portion of the solution with ether, which will be coloured yellow if an excess of alizarin is present. Warm the zirconium-alizarin solution on a water bath for 10 minutes and use the warm solution to impregnate the quantitative filter paper.

IV, 18. REACTIONS OF NITRATES, NO_3

Solubility.—All nitrates are soluble in water. The nitrates of mercury and bismuth yield basic salts on treatment with water; these are soluble in dilute nitric acid.

Use sodium nitrate, $NaNO_3$.

1. **Concentrated Sulphuric Acid**: reddish-brown vapours of nitrogen dioxide, accompanied by pungent acid vapours of nitric acid which fume in the air, are formed on heating the solid nitrate with the reagent. The nitric acid initially formed is decomposed by heating. Dilute sulphuric acid has no action (difference from nitrite).

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3;$$
$$4HNO_3 = 4NO_2 + O_2 + 2H_2O.$$

2. **Concentrated Sulphuric Acid and Bright Copper Turnings.**—On heating these with the solid nitrate, reddish-brown fumes of nitrogen dioxide are evolved, and the solution acquires a blue colour owing to the production of cupric nitrate. A solution of the nitrate may also be used; the sulphuric acid is then very cautiously added.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O\ ;$$
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$
$$2NO + O_2 = 2NO_2.$$

3. **Ferrous Sulphate Solution and Concentrated Sulphuric Acid (Brown Ring Test).**—This test is carried out in either of two ways: (*a*) Add 3 c.c. of a freshly prepared saturated solution of ferrous sulphate to 2 c.c. of the nitrate solution, and pour 3–5 c.c. of concentrated sulphuric acid slowly down the side of the test-tube so that the acid forms a layer beneath the mixture. A brown ring will form where the liquids meet. (*b*) Add 4 c.c. of concentrated sulphuric acid slowly to 2 c.c. of the nitrate solution, mix the liquids thoroughly and cool the mixture under a stream of cold water from the tap. Pour a saturated solution of ferrous sulphate slowly down the side of the tube so that it forms a layer on top of the liquid. A brown ring will form at the zone of contact of the two liquids.

The brown ring is due to the formation of the compound $[Fe(NO)]SO_4$. On shaking and warming the mixture the brown colour disappears, nitric oxide is evolved and a yellow solution of ferric sulphate remains. The test is unreliable in the presence of bromide, iodide, nitrite, chlorate and chromate (see Sect. **IV, 44**).

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3\ ;$$
$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O\ ;$$
$$FeSO_4 + NO = [Fe,NO]SO_4.$$

Bromides and iodides interfere because of the liberated halogen; the test is not trustworthy in the presence of chromates, sulphites, thiosulphates, iodates, cyanides, thiocyanates, ferro- and ferricyanides. All of these anions may be removed by adding excess of nitrate-free Ag_2SO_4 to an aqueous solution (or sodium carbonate extract), shaking vigorously for 3–4 minutes, and filtering the insoluble silver salts, etc.

Nitrites react similarly to nitrates. They are best removed by adding the solution to solid hydrazine sulphate; reaction takes place in the cold and the danger of slight oxidation of nitrite to nitrate is considerably reduced.

$$N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O.$$
$$N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O.$$

† The spot-test technique is as follows. Place a crystal of ferrous sulphate about as large as a pin head on a spot plate. Add a drop of the test solution and allow a drop of concentrated sulphuric acid to run in at the side of the drop. A brown ring forms round the crystal of ferrous sulphate.

Sensitivity: 2·5 μg. NO_3^-. Concentration limit: **1 in 25,000.**

4. **Aluminium or Zinc and Sodium Hydroxide Solution (Ammonia Test).**—Ammonia is evolved (detected by its odour and by mercurous nitrate paper) when a solution of a nitrate is boiled with zinc dust or gently warmed with aluminium powder and sodium hydroxide solution. Excellent results are obtained by the use of Devarda's alloy (45% Al, 5% Zn and 50% Cu). The reduction is due to the nascent hydrogen produced in the reaction. Ammonium ions must, of course, be removed by boiling the solution with sodium hydroxide solution before the addition of the metal.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2[ZnO_2] + 2H_2O.$$
$$3NaNO_3 + 8Al + 5NaOH + 2H_2O = 3NH_3 + 8Na[AlO_2].$$

Nitrites give a similar reaction and may be removed by the addition of sodium azide to the acid solution ; the solution is allowed to stand for a short time and then boiled in order to complete the reaction and to expel the readily volatile hydrogen azide :

$$HNO_2 + HN_3 = N_2 + N_2O + H_2O.$$

Other nitrogen compounds which evolve ammonia under the above conditions are cyanides, thiocyanates, ferrocyanides and ferricyanides. These may be removed by treating the aqueous solution (or a sodium carbonate extract) with excess of nitrate-free Ag_2SO_4, warming the mixture to about 60°, shaking vigorously for 3–4 minutes, and filtering from the silver salts of the interfering anions and excess of precipitant. The excess of silver ions is removed from the filtrate by adding an excess of NaOH solution, and filtering from the precipitated silver oxide. The filtrate is concentrated and tested with zinc, aluminium or Devarda's alloy.

Attention is directed to the fact that arsenites are reduced in alkaline solution by aluminium, Devarda's alloy, etc., to arsine, which blackens mercurous nitrate paper. Hence the mercurous nitrate test for ammonia is applicable only if arsenites be absent.

† The spot-test technique is carried out as follows. Place a drop of the test solution in the tube of Fig. 37, add 1–2 drops of 10 per cent sodium hydroxide solution and a few milligrams of Devarda's alloy. Place a watch glass with a drop of *p*-nitrobenzene-diazonium chloride reagent (for preparation, see under Ammonium, Section **III, 36,** reaction 7) on its under side upon the funnel stopper. Heat the apparatus gently for a short time. Add a tiny fragment of calcium oxide to the drop of the reagent : a red ring forms within 10–15 seconds.

Sensitivity : 10 μg. NO_3^-. Concentration limit : 1 in 5,000.

5. **Diphenylamine Reagent** ($C_6H_5.NH.C_6H_5$).—Pour the nitrate solution carefully down the side of the test-tube so that it forms a layer above the solution of the reagent ; a blue ring is formed at the zone of contact of the two liquids.

The test is a very sensitive one, but unfortunately is also given by a number of oxidising agents, such as nitrites, chlorates, bromates, iodates, permanganates, chromates, vanadates, molybdates and ferric salts.

The *reagent* is prepared by dissolving 0·5 g. of diphenylamine in 100 c.c. of concentrated sulphuric acid diluted with 20 c.c. of water.

6. **Nitron Reagent** (diphenyl-endo-anilo-dihydrotriazole $C_{20}H_{16}N_4$):* white crystalline precipitate of nitron nitrate $C_{20}H_{16}N_4,HNO_3$ with solutions of nitrates. Bromides, iodides, nitrites, chromates, chlorates, perchlorates, thiocyanates, oxalates and picrates also yield insoluble compounds, and hence the reaction is not very characteristic.

The *reagent* is prepared by dissolving 5 g. of nitron in 50 c.c. of 5% acetic acid.

7. **Action of heat.**—The result varies with the metal. The nitrates of sodium and potassium evolve oxygen (test with glowing splint) and leave solid nitrites (brown fumes with dilute acid); ammonium nitrate yields nitrous oxide and steam; the nitrates of the noble metals leave a residue of the metal, and a mixture of nitrogen dioxide and oxygen is evolved; the nitrates of the other metals, such as those of lead and copper, evolve oxygen and nitrogen dioxide, and leave a residue of the oxide.

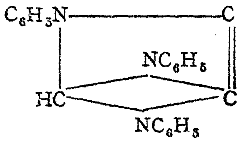
$$2NaNO_3 = 2NaNO_2 + O_2;$$
$$NH_4NO_3 = N_2O + 2H_2O;$$
$$2AgNO_3 = 2Ag + 2NO_2 + O_2;$$
$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

† *8.* **Reduction to Nitrite Test.**—Nitrates are reduced to nitrites by metallic zinc in acetic acid solution; the nitrite can be readily detected by means of the sulphanilic acid—α-naphthylamine reagent (see under Nitrites, Section **IV, 7,** reaction *10*). Nitrites, of course, interfere and are best removed with sodium azide in acid solution (see reaction *3* above).

Mix on a spot plate a drop of the neutral or acetic acid test solution with a drop of the sulphanilic acid reagent and a drop of the α-naphthylamine reagent, and add a few milligrams of zinc dust. A red colouration develops.

Sensitivity: 0·05 μg. NO_3^-. Concentration limit: 1 in 1,000,000.

* The constitution is:



IV, 19. **REACTIONS OF CHLORATES, ClO_3^-

Solubility.—All chlorates are soluble in water; potassium chlorate is one of the least soluble (66 g. per litre at 18°) and lithium chlorate one of the most soluble (3150 g. per litre at 18°).

*Use potassium chlorate, $KClO_3$.

1. **Concentrated Sulphuric Acid.**—All chlorates are decomposed with the formation of the greenish-yellow gas, chlorine dioxide ClO_2, which dissolves in the sulphuric acid to give an orange-yellow solution. On warming *gently* (*danger*) an explosive crackling occurs, which may develop into a violent explosion. In carrying out this test one or two small crystals of potassium chlorate (weighing not more than 0·1 gram) are treated with concentrated sulphuric acid in the cold; the yellow explosive chlorine dioxide can be seen on shaking the solution. The test-tube should not be warmed, and its mouth should be directed away from the student.

$$3KClO_3 + 3H_2SO_4 = 2ClO_2 + HClO_4 + 3KHSO_4 + H_2O.$$

2. **Concentrated Hydrochloric Acid.**—All chlorates are decomposed by this acid, and chlorine, together with varying quantities of the explosive chlorine dioxide, are evolved; the latter imparts a yellow colour to the acid. The mixture of gases is sometimes known as "euchlorine." The experiment should be conducted on a very small scale. The following two chemical reactions probably occur simultaneously:

$$2KClO_3 + 4HCl = 2ClO_2 + Cl_2 + 2H_2O + 2KCl;$$
$$KClO_3 + 6HCl = 3Cl_2 + 3H_2O + KCl.$$

3. **Barium Chloride Solution**: no precipitate. No precipitation occurs with silver nitrate solution.

4. **Sodium Nitrite Solution.**—On warming this reagent with a solution of the chlorate, the latter is reduced to a chloride, which may be identified by adding silver nitrate solution after acidification with dilute nitric acid. The nitrite must, of course, be free from chloride. A solution of sulphurous acid or of formaldehyde (10%; 1 part of formalin to 3 parts of water) acts similarly. Excellent results are obtained with zinc, aluminium or Devarda's alloy and sodium hydroxide solution (see under Nitrates, Section **IV, 18,** reaction *4*); the solution is acidified with dilute nitric acid after several minutes boiling,‡ and silver nitrate solution added.

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‡ It is best to filter off the excess of metal before adding the silver nitrate solution.

$$KClO_3 + 3NaNO_2 = KCl + 3NaNO_3.$$

$$KClO_3 + 3H_2SO_3 = KCl + 3H_2SO_4.$$

$$KClO_3 + 3H.CHO = KCl + 3H.COOH.$$

$$KClO_3 + 3Zn + 6NaOH = KCl + 3Na_2[ZnO_2] + 3H_2O.$$

$$KClO_3 + 2Al + 2NaOH = KCl + 2Na[AlO_2] + H_2O.$$

5. **Potassium Iodide Solution**: iodine is liberated if a mineral acid is present. If acetic acid is used, no iodine separates even on long standing (difference from iodate).

6. **Ferrous Sulphate Solution**: reduction to chloride upon boiling in the presence of dilute mineral acid (difference from perchlorate).

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O.$$

7. **Indigo Test.**—A dilute solution of indigo in concentrated sulphuric acid is added to the chlorate solution until the latter has a pale-blue colour. Dilute sulphurous acid or sodium sulphite solution is then added drop by drop; the blue colour is discharged. The chlorate is reduced by the sulphurous acid to chlorine or to hypochlorite, and the latter bleaches the indigo.

8. **Aniline Sulphate Test** $\{(C_6H_5.NH_2)_2H_2SO_4\}$.—A small quantity of the solid chlorate is mixed with 2 c.c. of concentrated sulphuric acid, and 2–3 c.c. of aqueous aniline sulphate solution added; a deep-blue colour is obtained (distinction from nitrate).

† *9.* **Manganous Sulphate-Phosphoric Acid Test.**—Manganous sulphate in syrupy phosphoric acid solution reacts with chlorates to form the violet-coloured mangani-phosphate ion:

$$6Mn^{++} + 12PO_4^{---} + 6H^+ + ClO_3^- = 6[Mn(PO_4)_2]^{---} + Cl^- + 3H_2O.$$

Persulphates and also periodates react similarly. The former may be decomposed by evaporating the sulphuric acid solution with a little silver nitrate as catalyst:

$$2H_2S_2O_8 + 2H_2O = 4H_2SO_4 + O_2.$$

The test cannot be applied in the presence of periodates.

Place a drop of the test solution in a small porcelain dish or capsule and add a drop of the reagent. Warm rapidly over a micro-burner and allow to cool. A violet colouration appears. Very pale colourations may be intensified by adding a drop of 1 per cent alcoholic diphenylcarbazide solution when a deep violet colour, due to an oxidation product of the diphenylcarbazide, is obtained.

Sensitivity: 0·05 μg. ClO_3^-. Concentration limit: 1 in 1,000,000.

The **reagent** is prepared by mixing equal volumes of saturated manganous sulphate solution and syrupy phosphoric acid.

10. **Action of Heat.**—All chlorates are decomposed by heat into chlorides and oxygen. Some perchlorate is usually formed as an intermediate product. The chloride is identified in the residue by extracting with water and adding dilute nitric acid and silver nitrate solution. An insoluble chlorate should be mixed with sodium carbonate before ignition.

$$2KClO_3 = 2KCl + 3O_2;$$
$$2KClO_3 = KClO_4 + KCl + O_2.$$

IV, 20. **REACTIONS OF BROMATES, BrO_3

Solubility.—Silver, barium and lead bromates are slightly soluble in water, the solubilities being respectively 2·0 g., 7·0 g. and 13·5 g. per litre at 20°; mercurous bromate is also sparingly soluble. Most of the other metallic bromates are readily soluble in water.

Use potassium bromate, $KBrO_3$.

1. **Concentrated Sulphuric Acid.**—Add 2 c.c. of the acid to 0·5 g. of the solid bromate; bromine and oxygen are evolved in the cold in consequence of the decomposition of the liberated bromic acid. The addition of carbon disulphide dissolves the bromine, forming a yellow solution.

$$4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O.$$

2. **Silver Nitrate Solution.**—A white crystalline precipitate of silver bromate $AgBrO_3$ is produced with a concentrated solution of a bromate. The precipitate is soluble in hot water, readily soluble in ammonium hydroxide solution forming a complex salt, and difficultly soluble in dilute nitric acid.

$$AgBrO_3 + 2NH_4OH = [Ag(NH_3)_2]BrO_3 + 2H_2O.$$

Precipitates of the corresponding bromates are also produced by the addition of solutions of barium chloride, lead acetate or mercurous nitrate to a concentrated solution of a bromate.

If the solution of silver bromate in ammonium hydroxide solution is treated dropwise with sulphurous acid solution, silver bromide separates: the latter dissolves in concentrated ammonium hydroxide solution (difference from iodate).

3. **Sulphur Dioxide.**—If the gas is bubbled through a solution of a bromate, the latter is reduced to a bromide (see

Bromides, Section **IV, 15**). A similar result is obtained with hydrogen sulphide and with sodium nitrite solution (see under Chlorates, Section **IV, 19**, reaction *4*).

$$KBrO_3 + 3H_2SO_3 = KBr + 3H_2SO_4.$$

$$KBrO_3 + 3H_2S = KBr + 3H_2O + 3S.$$

$$KBrO_3 + 3NaNO_2 = KBr + 3NaNO_3.$$

4. **Hydrobromic Acid.**—Mix together solutions of potassium bromate and bromide, and acidify with dilute sulphuric acid; bromine is liberated as a result of interaction between the bromic and hydrobromic acids set free. The bromine may be extracted by adding a little carbon disulphide, chloroform or carbon tetrachloride.

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

5. **Action of Heat.**—Potassium bromate on heating evolves oxygen and a bromide remains. No perbromate is formed. Sodium and calcium bromates behave similarly, but cobalt, zinc and other similar metallic bromates evolve oxygen and bromine, and leave an oxide.

6. **Manganous Sulphate Test.**—If a bromate solution is treated with a little of a 1 : 1 mixture of saturated manganous sulphate solution and 2*N*-sulphuric acid, a red colouration is produced. Upon rapidly concentrating the solution, brown hydrated manganese dioxide separates, which is insoluble in dilute sulphuric acid but dissolves in a mixture of dilute sulphuric and oxalic acids (difference from chorates and also iodates, which neither give the colouration nor yield the brown precipitate).

The reaction may be used as a spot test.

IV, 21. **REACTIONS OF IODATES, IO_3^-

Solubility.—The iodates of the alkali metals are soluble in water; those of the other metals are sparingly soluble and, in general, less soluble than the corresponding chlorates and bromates. Some solubilities in grams per litre at 20° are: lead iodate 0·03 (25°), silver iodate 0·06, barium iodate 0·22, calcium iodate 3·7, potassium iodate 81·3 and sodium iodate 90·0. Iodic acid is a crystalline solid, and has a solubility of 2330 g. per litre at 20°.

Use potassium iodate, KIO_3.

1. **Concentrated Sulphuric Acid**: no action in the absence of reducing agents; readily converted into hydriodic acid in the presence of ferrous sulphate.

$$HIO_3 + 6FeSO_4 + 3H_2SO_4 = HI + 3Fe_2(SO_4)_3 + 3H_2O.^*$$

* Iodine will eventually separate owing to the interaction between the hydriodic and iodic acid (see reaction *6* below).

2. **Silver Nitrate Solution** : white curdy precipitate of silver iodate $AgIO_3$, readily soluble in ammonium hydroxide solution, but difficulty soluble in dilute nitric acid.

$$KIO_3 + AgNO_3 = AgIO_3 + KNO_3;$$
$$AgIO_3 + 2NH_3 = [Ag(NH_3)_2]IO_3.$$

If the ammoniacal solution of the precipitate is treated dropwise with sulphurous acid solution, silver iodide is precipitated; the latter is not dissolved by concentrated ammonium hydroxide solution (difference from bromate).

3. **Barium Chloride Solution** : white precipitate of barium iodate $Ba(IO_3)_2$ (difference from chlorate), difficultly soluble in hot water and in dilute nitric acid, but insoluble in alcohol (difference from iodide). If the precipitate of barium iodate is well washed, treated with a little sulphurous acid solution and 1–2 c.c. of carbon disulphide or carbon tetrachloride, the latter is coloured violet by the liberated iodine.

$$2KIO_3 + BaCl_2 = Ba(IO_3)_2 + 2KCl.$$

4. **Mercuric Chloride Solution** : white precipitate of mercuric iodate $Hg(IO_3)_2$ (difference from chlorate and bromate). Lead acetate solution similarly gives a precipitate of lead iodate $Pb(IO_3)_2$.

$$2KIO_3 + HgCl_2 = Hg(IO_3)_2 + 2KCl.$$

5. **Sulphur Dioxide or Hydrogen Sulphide.**—Passage of sulphur dioxide or of hydrogen sulphide into a solution of an iodate, acidified with dilute hydrochloric acid, liberates iodine, which may be recognised by the addition of starch solution or of carbon disulphide, chloroform or carbon tetrachloride. With an excess of either reagent, the iodine is further reduced to hydriodic acid.

$$KIO_3 + HCl = HIO_3 + KCl;$$
$$2HIO_3 + 5H_2SO_3 = I_2 + 5H_2SO_4 + H_2O;$$
$$I_2 + H_2SO_3 + H_2O \rightleftharpoons 2HI + H_2SO_4.$$
$$2HIO_3 + 5H_2S = I_2 + 5S + 6H_2O;$$
$$I_2 + H_2S \rightleftharpoons 2HI + S.$$

6. **Potassium Iodide Solution.**—Mix together solutions of potassium iodide and potassium iodate, and acidify with acetic acid or with tartaric acid solution; iodine is immediately liberated (use chloroform or carbon tetrachloride test).

$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

7. **Action of Heat.**—The alkali iodates decompose into oxygen and an iodide. Most iodates of the divalent metals yield iodine and oxygen and leave a residue of oxide ; barium iodate, exceptionally, gives the periodate.

$$2KIO_3 = 2KI + 3O_2 ;$$
$$2Pb(IO_3)_2 = I_2 + 5O_2 + 2PbO ;$$
$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

†*8.* **Hypophosphorous Acid-Starch Solution Test.**—Iodates are reduced by hypophosphorous acid eventually to iodides. The reaction takes place in three stages :

$$IO_3^- + 3H_3PO_2 = I^- + 3H_3PO_3 \quad \text{(i)};$$
$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \quad \text{(ii)};$$
$$I_2 + H_3PO_3 + H_2O = 2HI + H_3PO_4 \quad \text{(iii)}.$$

The first two stages are rapid and the third stage is a slow reaction. The iodine can be readily identified by the starch reaction. Chlorates and bromates do not react under these conditions.

Place a drop of the neutral test solution on a spot plate and mix it with a drop of starch solution (for preparation, see under Iodides, Section **IV, 16,** reaction *9*) and a drop of a dilute solution of hypophosphorous acid. A transitory blue colouration is produced.

Sensitivity : 1 μg. IO_3^-. Concentration limit : 1 in 50,000.

† *9.* **Potassium Thiocyanate Test.**—Iodates react with thiocyanates in acid solution with the liberation of iodine :

$$6IO_3^- + 5CNS^- + 6H^+ + 2H_2O = 3I_2 + 5HCN + 5HSO_4^-.$$

Treat a piece of starch paper successively with a drop of 5 per cent potassium thiocyanate solution and a drop of the acid test solution. A blue spot is obtained.

Sensitivity : 3 μg. IO_3^-. Concentration limit : 1 in 12,000.

IV, 22. **REACTIONS OF PERCHLORATES, ClO_4^-

Solubility.—The perchlorates are generally soluble in water. Potassium perchlorate is one of the least soluble (7·5 g. and 218 g. per litre at 0° and 100° respectively), and sodium perchlorate is one of the most soluble (2096 g. per litre at 25°).

Use sodium perchlorate, $NaClO_4$.

1. **Concentrated Sulphuric Acid** : no visible action with the solid salt although the free perchloric acid $HClO_4$ is liberated ; on strong heating, white fumes of the hydrate, $HClO_4,H_2O$, are evolved.

$$NaClO_4 + H_2SO_4 = HClO_4 + NaHSO_4.$$

2. **Potassium Chloride Solution** : white precipitate of potassium perchlorate $KClO_4$, insoluble in alcohol (see under

Potassium, Section **III, 34**, reaction *3*). Ammonium chloride solution gives a similar white precipitate of ammonium perchlorate NH_4ClO_4.

3. **Barium Chloride Solution**: no precipitate. A similar result is obtained with silver nitrate solution.

4. **Indigo Test**: no decolourisation even in the presence of acid (difference from hypochlorite and chlorate).

5. **Sulphur Dioxide or Hydrogen Sulphide or Ferrous Salts**: no reduction (difference from chlorate).

6. **Titanous Sulphate Solution**: reduced to chloride.

7. **Action of Heat**: oxygen is evolved, and a chloride (for tests see under Chlorides, Section **IV, 14**) is produced.

$$NaClO_4 = NaCl + 2O_2.$$

IV, 23.**REACTIONS OF BORATES, BO_3^{---}, $B_4O_7^{--}$, BO_2^{-}

The borates are derived from the three boric acids: ortho-boric acid H_3BO_3, pyro-boric acid $H_2B_4O_7$ and meta-boric acid HBO_2. Ortho-boric acid is a white crystalline solid, sparingly soluble in cold but more soluble in hot water; very few salts of this acid are definitely known. On heating ortho-boric acid at 100°, it is converted into meta-boric acid; at 140° pyro-boric acid is produced. Most of the salts are derived from the meta- and pyro-acids. Owing to the weakness of boric acid, the soluble salts are hydrolysed in solution and therefore react alkaline.

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3;$$
$$NaBO_2 + H_2O \rightleftharpoons NaOH + H_3BO_3.$$

Solubility.—The borates of the alkali metals are readily soluble in water. The borates of the other metals are, in general, difficultly soluble in water, but fairly soluble in acids and in ammonium chloride solution.

Use sodium pyro-borate ("borax"), $Na_2B_4O_7,10H_2O$.

1. **Concentrated Sulphuric Acid**: no visible action in the cold, although ortho-boric acid H_3BO_3 is set free. On heating, however, white fumes of boric acid are evolved. If concentrated hydrochloric acid is added to a concentrated solution of borax, boric acid is precipitated.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4.$$
$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

2. **Concentrated Sulphuric Acid and Alcohol (Flame Test).**—If a little borax is mixed with 1 c.c. of concentrated sulphuric acid and 5 c.c. of methyl or ethyl alcohol (the former is to be preferred owing to its greater volatility) in a small porcelain basin, and the alcohol ignited, the latter will burn with a green-edged flame, due to the formation of methyl borate $B(OCH_3)_3$ or of ethyl borate $B(OC_2H_5)_3$. Copper and barium salts may give a similar green flame. The following modification of the test, which depends upon the greater volatility of boron trifluoride BF_3, can be used in the presence of copper and barium compounds; these do not form volatile compounds under the following experimental conditions. Thoroughly mix the borate with powdered calcium fluoride and a little concentrated sulphuric acid, and bring a little of the paste thus formed on the loop of a platinum wire, or upon the end of a glass rod, very *close* to the edge of the base of a Bunsen flame without actually touching it; volatile boron trifluoride is formed and colours the flame green.

$$H_3BO_3 + 3CH_3OH \rightleftharpoons B(OCH_3)_3 + 3H_2O.$$

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF;$$

$$Na_2B_4O_7 + H_2SO_4 \rightleftharpoons 2B_2O_3 + Na_2SO_4 + H_2O;$$

$$B_2O_3 + 6HF \rightleftharpoons 2BF_3 + 3H_2O.$$

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† The reaction may be adapted as a spot test in the following manner. The methyl borate is distilled off and passed into an aqueous solution containing potassium fluoride, manganous nitrate and silver nitrate. The ester is hydrolysed by the water to boric acid:

$$B(OCH_3)_3 + 3H_2O = H_3BO_3 + 3CH_3OH;$$

the boric acid reacts with the alkali fluoride forming a borofluoride and liberating free caustic alkali:

$$H_3BO_3 + 4KF = K[BF_4] + 3KOH;$$

the free caustic alkali is identified by the formation of a black precipitate with manganous nitrate-silver nitrate solution (see under Ammonium, Section **III, 36,** reaction *8*):

$$Mn^{++} + 2Ag^+ + 4OH^- = MnO_2 + 2Ag + 2H_2O.$$

Place a drop of the alkaline test solution in the distillation apparatus of Fig. 40, and evaporate to dryness. Add 5 drops of concentrated sulphuric acid and 5 drops of pure methyl alcohol, stopper the apparatus and heat to 80°C in a water bath. Collect the methyl borate which distils over in a micro-porcelain crucible, waxed on the inside, and containing about 1 c.c. of the reagent. A black precipitate forms. For very small amounts of borate it is best to add a few drops of benzidine acetate solution and thus to detect the traces of manganese dioxide by the resultant blue colour.

Sensitivity: 0·01 μg. B. Concentration limit: 1 in 5,000,000.

The **reagent** (a manganese nitrate-silver nitrate solution containing potassium fluoride) is prepared as follows. Dissolve 2·87 g. of manganous nitrate and 1·69 g. of silver nitrate in 100 c.c. of water, add a drop of dilute alkali and filter the solution from the black precipitate. Treat the filtrate with a solution of 3·5 g. of potassium fluoride in 50 c.c. of water; a white precipitate will form which on heating becomes grey and black. Boil, filter and use the clear solution as the reagent.

3. **Turmeric Paper Test.**—If a piece of turmeric paper is dipped into a solution of a borate acidified with dilute hydrochloric acid and then dried, it becomes reddish-brown. The drying of the paper is most simply carried out by winding it on the outside near the rim of a test-tube containing water, and boiling the water for 2–3 minutes. On moistening the paper with dilute sodium or ammonium hydroxide solution, it becomes bluish-black or greenish-black. Chromates, chlorates, nitrites, and other oxidising agents interfere because of their bleaching action on the turmeric.

4. **Silver Nitrate Solution** : white precipitate of silver metaborate $AgBO_2$ from fairly concentrated borax solution, soluble in both ammonium hydroxide solution and in acetic acid. On boiling the precipitate with water, it is completely hydrolysed and a brown precipitate of silver oxide is obtained. A brown precipitate of silver oxide is produced directly in very dilute solutions.

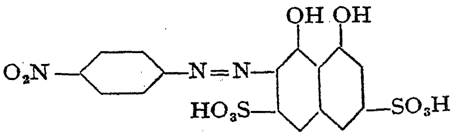
$$Na_2B_4O_7 + 3H_2O + 2AgNO_3 = 2AgBO_2 + 2H_3BO_3 + 2NaNO_3 ;$$
$$2AgBO_2 + 3H_2O = Ag_2O + 2H_3BO_3.$$

5. **Barium Chloride Solution** : white precipitate of barium meta-borate $Ba(BO_2)_2$ from fairly concentrated solutions; the precipitate is soluble in excess of the reagent, in dilute acids and in solutions of ammonium salts. Solutions of calcium and strontium chloride behave similarly.

$$Na_2B_4O_7 + 3H_2O + BaCl_2 = Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl.$$

6. **Action of Heat.**—Powdered borax when heated in an ignition tube, or upon a platinum wire, swells up considerably, and then subsides, leaving a colourless glass of the anhydrous salt. The glass possesses the property of dissolving many oxides on heating, forming meta-borates, which often have characteristic colours. This is the basis of the borax bead test for various metals (see Section **II, 1**, reaction *5*).

† *7.* **para-Nitrobenzene-azo-chromotropic Acid* Reagent**



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* Alternative names are : *p*-nitrobenzene-azo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid and chromotrope 2B (the latter is the sodium salt).

Borates cause the blue-violet reagent to assume a greenish-blue colour.

Evaporate a drop of the slightly alkaline solution to dryness in a small porcelain dish or capsule. Stir the warm residue with 2–3 drops of the reagent. A greenish-blue colouration is obtained on cooling. A blank test should be performed simultaneously.

Sensitivity: 0·1 μg. B. Concentration limit: 1 in 500,000.

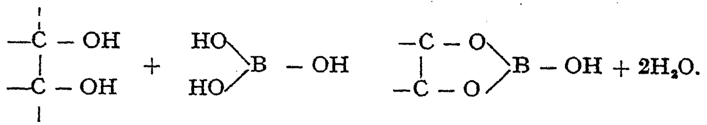
Oxidising agents and fluorides interfere, the latter because of the formation of borofluorides. Oxidising agents, including nitrates and chlorates, are rendered innocuous by evaporating with solid hydrazine sulphate, whilst fluorides may be removed as silicon tetrafluoride by evaporation with silicic acid and sulphuric acid.

The experimental details are as follows. Treat 2 drops of the test solution in a small porcelain crucible either with a little solid hydrazine sulphate or with a few specks of silicic acid and 1–2 drops of concentrated sulphuric acid, and heat cautiously until fumes of sulphuric acid appear. Add 3–4 drops of the reagent whilst the residue is still warm and observe the colour on cooling.

Sensitivity: 0·25 μg. B in the presence of 12,000 times the amount of $KClO_3$ or KNO_3; 0·5 μg. B in the presence of 2,500 times the amount of NaF.

The **reagent** consists of a 0·005 per cent solution of chromotrope 2B in concentrated sulphuric acid.

8. **Mannitol-Bromothymol Blue Test.**—Boric acid acts as a very weak monobasic acid ($K_a = 5{\cdot}8 \times 10^{-10}$), but upon the addition of certain organic poly-hydroxy compounds, such as mannitol (mannite), glycerol, dextrose or invert sugar, it is transformed into a relatively strong acid, probably of the type:



The pH of the solution therefore decreases. Hence if the solution is initially almost neutral to, say, bromothymol blue (green), then upon the addition of mannitol the colour becomes yellow. It is advisable when testing for minute quantities of borates to recrystallise the mannitol from a solution neutralised to bromothymol blue, wash with pure acetone and dry at 100°C.

Render the test solution almost neutral to bromothymol blue by treating it with acid or alkali solution until the indicator turns green. Place 2 drops of the test solution (treated as above) on a spot plate and add a few milligrams of mannitol or 1 drop of the 50 per cent aqueous solution. A yellow colouration is obtained. It is advisable to carry out a blank test with distilled water simultaneously.

Sensitivity: 0·001 μg. B (in 0·03 c.c.). Concentration limit: 1 in 30,000,000.

IV, 24. REACTIONS OF SULPHATES, SO_4^{--}

Solubility.—The sulphates of barium, strontium and lead are practically insoluble in water,* those of calcium and mercuric mercury are slightly soluble, and most of the remaining metallic sulphates are soluble. Some basic sulphates, such as those of mercury, bismuth and chromium, are also insoluble in water, but these dissolve in dilute hydrochloric or nitric acid.

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* Of these three sulphates, that of strontium is the most soluble.

Sulphuric acid is a colourless, oily and hygroscopic liquid, of specific gravity 1·838. The pure, commercial, concentrated acid is a constant boiling point mixture, boiling point 338° and containing *ca.* 98% of acid. It is miscible with water in all proportions with the evolution of considerable heat; on mixing the two, the acid should always be poured in a thin stream into the water (if the water is poured into the heavier acid, steam may be suddenly generated which will carry with it some of the acid and may therefore cause considerable damage).

Use sodium sulphate, $Na_2SO_4,10H_2O$.

1. **Barium Chloride Solution**: white precipitate of barium sulphate $BaSO_4$ (see under Barium, Section **III, 29**), insoluble in warm dilute hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, concentrated hydrochloric acid. The test is usually carried out by adding the reagent to the solution acidified with dilute hydrochloric acid; carbonates, sulphites and phosphates are not precipitated under these conditions. Concentrated hydrochloric acid or concentrated nitric acid should not be used, as a precipitate of barium chloride or of barium nitrate may form; these dissolve, however, upon dilution with water. The barium sulphate precipitate may be filtered from the hot solution and fused on charcoal with sodium carbonate, when sodium sulphide will be formed. The latter may be extracted with water, and the extract filtered into a freshly prepared solution of sodium nitroprusside, when a transient, purple colouration is obtained (see under Sulphides, Section **IV, 6**, reaction *5*). An alternative method is to add a few drops of very dilute hydrochloric acid to the fused mass, and to cover the latter with lead acetate paper; a black stain of lead sulphide is produced on the paper. The so-called *Hepar reaction*, which is less sensitive than the above two tests, consists in placing the fusion product on a silver coin and moistening with a little water; a brownish-black stain of silver sulphide results.

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl;$$

$$BaSO_4 + Na_2CO_3 + 4C = Na_2S + BaCO_3 + 4CO;$$

$$2Na_2S + 4Ag + O_2 + 2H_2O = 2Ag_2S + 4NaOH.$$

A more efficient method for decomposing most sulphur compounds consists in heating them with sodium or potassium, and then testing the solution of the product for sulphide. The test is rendered sensitive by heating the substance with potassium in a capillary tube, dissolving the melt in water, and testing for sulphide by the nitroprusside or methylene blue reactions (see under Sulphides, Section **IV, 6,** reactions *6* and *7*).

The reader is warned that the above tests (depending upon the formation of a sulphide) are not exclusive to sulphates but are given by most sulphur compounds. If, however, the barium sulphate precipitated in the presence of hydrochloric acid is employed, then the reaction may be employed as a confirmatory test for sulphates.

2. **Lead Acetate Solution** : white precipitate of lead sulphate $PbSO_4$, soluble in hot concentrated sulphuric acid, in solutions of ammonium acetate and of ammonium tartrate (see under Lead, Section **III, 2,** reaction *3*), and in sodium hydroxide solution. In the last case sodium plumbite is formed, and on acidification with hydrochloric acid, the lead crystallises out as the chloride. If any of the aqueous solutions of the precipitate are acidified with acetic acid and potassium chromate solution added, yellow lead chromate is precipitated (see under Lead, *loc. cit.*).

$$Pb(C_2H_3O_2)_2 + Na_2SO_4 = PbSO_4 + 2Na.C_2H_3O_2.$$

3. **Silver Nitrate Solution** : white, crystalline precipitate of silver sulphate Ag_2SO_4 (solubility 5·8 g. per litre at 18°) from concentrated solutions.

$$Na_2SO_4 + 2AgNO_3 = Ag_2SO_4 + 2NaNO_3.$$

† *4.* **Sodium Rhodizonate Test.**—Barium salts yield a reddish-brown precipitate with sodium rhodizonate (see under Barium, Section **III, 29,** reaction *7*). Sulphates and sulphuric acid cause immediate decolourisation because of the formation of insoluble barium sulphate. This test is specific for sulphates.

Place a drop of barium chloride solution upon filter or drop-reaction paper, followed by a drop of a freshly-prepared aqueous solution of sodium rhodizonate. Treat the reddish-brown spot with a drop of the acid or alkaline test solution. The coloured spot disappears.

IV, 25. **REACTIONS OF PERSULPHATES, $S_2O_8^{--}$

Solubility.—The best known persulphates, those of sodium, potassium, ammonium and barium, are soluble in water, the potassium salt being the least soluble (17·7 g. per litre at 0°).

Use ammonium persulphate, $(NH_4)_2S_2O_8$.

1. **Water.**—All persulphates are decomposed on boiling with water into the sulphate, free sulphuric acid and oxygen. The oxygen contains appreciable quantities of ozone, which may be detected by its odour or by its property of turning starch-iodide paper blue. A similar result is obtained with dilute sulphuric or nitric acid. With dilute hydrochloric acid, chlorine is evolved (see reaction *4* below). By dissolving the solid persulphate in concentrated sulphuric acid at 0°, permonosulphuric acid (Caro's acid) H_2SO_5 is formed in solution; this possesses strong oxidising properties.

$$2(NH_4)_2S_2O_8 + 2H_2O = 2(NH_4)_2SO_4 + 2H_2SO_4 + O_2.$$
$$O_3 + 2KI + H_2O = I_2 + O_2 + 2KOH.$$

2. **Silver Nitrate Solution**: black precipitate of silver peroxide Ag_2O_2 from concentrated solutions. If only a little silver nitrate solution be added and then ammonium hydroxide solution, the silver peroxide, or the silver ion, acts catalytically leading to the evolution of nitrogen and the liberation of considerable heat.

$$(NH_4)_2S_2O_8 + 2AgNO_3 + 2H_2O = Ag_2O_2 + 2NH_4HSO_4 + 2HNO_3.$$
$$8NH_4OH + 3(NH_4)_2S_2O_8\ (+ Ag) = N_2 + 6(NH_4)_2SO_4 + 8H_2O\ (+Ag).$$

3. **Barium Chloride Solution**: no immediate precipitate in the cold with a solution of a pure persulphate; on standing for some time or on boiling, a precipitate of barium sulphate is obtained, due to the decomposition of the persulphate.

4. **Potassium Iodide Solution**: iodine is slowly liberated in the cold and rapidly on warming (test with starch solution). Ferrous sulphate solution is oxidised to ferric sulphate.

$$(NH_4)_2S_2O_8 + 2KI = I_2 + (NH_4)_2SO_4 + K_2SO_4.$$

5. **Manganous Sulphate Solution**: brown precipitate, MnO_2,H_2O or H_2MnO_3, in neutral or preferably alkaline (sodium hydroxide) solution. In nitric acid solution and in the presence of a little silver nitrate (which acts catalytically, see reaction *2* above), permanganic acid is formed on warming.

$$MnSO_4 + (NH_4)_2S_2O_8 + 3H_2O = H_2MnO_3 + (NH_4)_2SO_4 + 2H_2SO_4;$$
$$2MnSO_4 + 5H_2S_2O_8 + 8H_2O = 2HMnO_4 + 12H_2SO_4.$$

6. **Potassium Permanganate Solution**: unaffected (distinction from hydrogen peroxide). It is also unaffected by a solution of titanous sulphate.

IV, 26. **REACTIONS OF SILICATES, SiO_3^{--}

The silicic acids may be represented by the general formula $xSiO_2$, yH_2O. Salts corresponding to ortho-silicic acid H_4SiO_4 ($SiO_2, 2H_2O$) meta-silicic acid H_2SiO_3 (SiO_2, H_2O) and di-silicic acid $H_2Si_2O_5$($2SiO_2$, H_2O) are definitely known. The meta-silicates are sometimes designated simply as silicates.

Solubility.—Only the silicates of the alkali metals are soluble in water; they are hydrolysed in aqueous solution and therefore react alkaline.

$$Na_2SiO_3 + 2H_2O \rightleftharpoons 2\,NaOH + H_2SiO_3.$$

Use a solution of water glass; this contains, largely, sodium meta-silicate Na_2SiO_3.

1. **Dilute Hydrochloric Acid.**—Add dilute hydrochloric acid to the solution of the silicate; a gelatinous precipitate of meta-silicic acid is obtained, particularly on boiling. The precipitate is insoluble in concentrated acids. The freshly precipitated substance is appreciably soluble in water and in dilute acids. It is converted by repeated evaporation with concentrated hydrochloric acid on the water bath into a white insoluble powder (silica SiO_2).

If a dilute solution (say, 1–10%) of water glass is quickly added to moderately concentrated hydrochloric acid, no precipitation of silicic acid takes place; it remains in colloidal solution (sol).

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl.$$

2. **Ammonium Chloride or Ammonium Carbonate Solution**: gelatinous precipitate of silicic acid. This reaction is important in routine qualitative analysis since silicates, unless previously removed, will be precipitated by ammonium chloride solution in Group IIIA.

$$Na_2SiO_3 + 2NH_4Cl + 2H_2O = H_2SiO_3 + 2NaCl + 2NH_4OH.$$

$$Na_2SiO_3 + (NH_4)_2CO_3 + 2H_2O = H_2SiO_3 + Na_2CO_3 + 2NH_4OH.$$

The reaction consists essentially in the removal of the hydroxyl ions, produced as a result of hydrolysis (Section **I, 40**), by the ammonium ion to form the feebly dissociated ammonium hydroxide.

$$Na_2SiO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2SiO_3.$$

3. **Silver Nitrate Solution**: yellow precipitate of silver silicate Ag_2SiO_3, soluble in dilute acids and in dilute ammonium hydroxide solution.

$$Na_2SiO_3 + 2AgNO_3 = Ag_2SiO_3 + 2NaNO_3.$$

4. **Barium Chloride Solution**: white precipitate of barium silicate $BaSiO_3$, soluble in dilute nitric acid. Calcium chloride solution gives a similar precipitate of calcium silicate.

$$Na_2SiO_3 + BaCl_2 = BaSiO_3 + 2NaCl.$$

5. **Ammonium Molybdate Solution and Stannous Chloride Solution.**—This is an extremely sensitive test and is applicable to all soluble silicates. A blank test must first be performed in order to confirm the absence of silicates in the reagents employed. The solution is treated with 10 c.c. of a 10% solution of ammonium molybdate (free from nitric acid; see Section **VII, 2,** method of preparation *B*) and dilute hydrochloric acid slowly added until the solution is faintly acid; a few c.c. of stannous chloride solution or preferably of sodium stannite solution (prepared by adding excess of sodium hydroxide solution to stannous chloride solution) is then added, whereupon a deep blue colouration develops. Phosphates and arsenates interfere and must be removed before applying the test (compare reaction *7* below).

6. **Microcosmic Salt Bead Test.**—Most silicates, and also silica, when fused in a bead of microcosmic salt, $Na(NH_4)HPO_4,4H_2O$, in a loop of platinum wire give this test. The microcosmic salt first fuses to a transparent bead consisting largely of sodium meta-phosphate (see Section **II, 1,** reaction *6*); when a minute quantity of the solid silicate or even of the solution is introduced into the bead (best by dipping the hot bead into the substance) and the whole again heated, the silica produced will not dissolve in the bead, but will swim about in the fused mass, and is visible as white opaque masses or " skeletons " in both the fused and the cold bead.

$$CaSiO_3 + NaPO_3 = CaNaPO_4 + SiO_2.$$

Insoluble silicates are best brought into solution by fusing the powdered solid, mixed with 6 times its weight of fusion mixture, in a platinum crucible* or upon platinum foil; the alkali carbonates react with the silicate yielding an alkali silicate. The cold mass is then evaporated to dryness on the water bath with excess of dilute hydrochloric acid; the alkali silicate is thereby first decomposed yielding gelatinous silicic acid and ultimately into white, amorphous silica, whilst the metallic oxides derived from the insoluble silicate are converted into chlorides. The residue is extracted with boiling dilute hydrochloric acid; this removes the metals as chlorides and insoluble silica remains behind. A simpler, but not quantitative, method is to extract the fusion mixture melt with boiling water: sufficient sodium or potassium silicate passes into solution to give any of the reactions referred to above.

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* A nickel or iron crucible should be used if metals of Group I or II are likely to be present.

When the insoluble silicate has to be tested for alkali metals also, the ollowing "**tetrafluoride test**" is more convenient. About 1 gram of the substance is mixed with 0·5 gram of calcium fluoride in a platinum (or lead) crucible and sufficient concentrated sulphuric acid added to form a thin paste; the contents of the crucible are mixed with the aid of a stout platinum wire, and a moist watch glass (or a platinum crucible cover, if this is available) with a drop of water hanging from the convex surface placed over the crucible. On gently warming the crucible and examining the water, it will be found to have become turbid, due to the hydrolysis of the silicon tetrafluoride initially formed to gelatinous silicic acid. The watch glass should not be left too long in contact with the vapours, since the turbidity disappears with excess of hydrogen fluoride.

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$

† 7. **Ammonium Molybdate-Benzidine Test.**—Silicates react with molybdates in acid solution to form the complex silico-molybdic acid $H_4[SiMo_{12}O_{40}]$, of which the ammonium salt, unlike the analogous phosphoric acid and arsenic acid compounds, is soluble in water and acids to give a yellow solution. The test depends upon the reaction between silico-molybdic acid and benzidine in acetic acid solution whereby "molybdenum blue" and a blue quinonoid oxidation compound of benzidine are produced.

Place a drop of the test solution and of the molybdate reagent upon drop reaction paper, and warm gently over a wire gauze. Add a drop of the benzidine reagent and hold the paper over ammonia vapour. A blue colouration results.

Sensitivity: 1 μg. SiO_2. Concentration limit: 1 in 50,000.

A better method for conducting the test is the following. Place a drop of the slightly acid test solution (the acidity should not exceed 0·5N) in a small porcelain crucible of good quality, and add a drop of the molybdate reagent. Warm cautiously over a wire gauze (or upon a sheet of asbestos resting upon a hot plate) until bubbles escape. Cool, add a drop of the benzidine reagent followed by a drop of saturated sodium acetate solution. A blue colour is obtained. It is essential to carry out a blank test with a drop of water and a drop of the molybdate reagent in another crucible of similar quality.

Sensitivity: 0·1 μg. SiO_2. Concentration limit: 1 in 500,000.

Phosphoric and arsenic acids form compounds analogous to silico-molybdic acid which also react with benzidine with colour formation, hence these acids should be removed before applying the test. In the **presence of phosphoric acid,** the test is carried out as follows. Mix a drop of the test solution with 2 drops of the molybdate reagent in a micro-centrifuge tube and centrifuge the mixture. Transfer the supernatant liquid to a micro-crucible by means of a capillary tube, warm gently, cool, and add 2 drops of 1 per cent oxalic acid solution (the latter decomposes the small quantity of residual phosphomolybdate $(NH_4)_3[PMo_{12}O_{40}]$ but has little action on the silico-molybdic acid complex), then introduce a drop of the benzidine reagent and 2–3 drops of saturated sodium acetate solution. A blue colour forms.

Sensitivity: 6 μg. SiO_2 in the presence of 250 times the amount of P_2O_5. Concentration limit: 1 in 8,000.

The **ammonium molybdate reagent** is prepared by dissolving 5 g. of ammonium molybdate in 100 c.c. of cold water and pouring into 35 c.c. of nitric acid (sp. gr. 1·2).

The **benzidine reagent** is made by dissolving 0·05 g. of benzidine or its hydrochloride in 10 c.c. of glacial acetic acid and diluting with water to 100 c.c.

IV, 27. **REACTIONS OF SILICOFLUORIDES (FLUOSILICATES), $[SiF_6]^{--}$

Solubility.—Most metallic silicofluorides, with the exception of the barium and potassium salts which are sparingly soluble, are soluble in water. A solution of the acid (hydrofluosilicic acid $H_2[SiF_6]$) is one of the products of the action of water upon silicon tetrafluoride, and is also formed by dissolving silica in hydrofluoric acid.

$$SiO_2 + 6HF = H_2[SiF_6] + 2H_2O.$$

Use sodium silicofluoride, $Na_2[SiF_6]$.

1. **Concentrated Sulphuric Acid**: silicon fluoride and hydrogen fluoride are evolved on warming the reagent with the solid salt. If the reaction is carried out in a platinum or lead crucible, the escaping gas will etch glass and will cause a drop of water to become turbid (see under Silicates, Section **IV, 26,** reaction *6*).

$$Na_2[SiF_6] + H_2SO_4 = SiF_4 + 2HF + Na_2SO_4.$$

2. **Barium Chloride Solution**: white crystalline precipitate of barium silicofluoride $Ba[SiF_6]$, sparingly soluble in water (0·27 g. per litre at 17°) and insoluble in dilute hydrochloric acid. The precipitate is distinguished from barium sulphate by the evolution of hydrogen fluoride and silicon fluoride, which etch glass, on heating with concentrated sulphuric acid in a lead crucible.

$$Na_2[SiF_6] + BaCl_2 = Ba[SiF_6] + 2NaCl.$$

3. **Potassium Chloride Solution**: white, gelatinous precipitate of potassium silicofluoride $K_2[SiF_6]$ from concentrated solutions. The precipitate is slightly soluble in water (1·20 g. per litre at 17°), less soluble in excess of the reagent and in 50% alcohol.

4. **Ammonium Hydroxide Solution**: decomposition occurs with the separation of gelatinous silicic acid.

$$Na_2[SiF_6] + 4NH_4OH = H_4SiO_4 + 2NaF + 4NH_4F.$$

5. **Action of Heat**: decomposition occurs into silicon tetrafluoride, which renders a drop of water turbid, and the metallic fluoride, which can be tested for in the usual manner (see under Fluorides, Section **IV, 17**).

$$Na_2[SiF_6] = SiF_4 + 2NaF.$$

IV, 28. REACTIONS OF ORTHOPHOSPHATES, PO_4^{---}

Three phosphoric acids are known: ortho- H_3PO_4, pyro- $H_4P_2O_7$, and metaphosphoric acid HPO_3. Salts of the three acids exist; the orthophosphates are the most stable and incidentally the most important*; the pyro- and metaphosphates pass into orthophosphates slowly at the ordinary temperature, and more rapidly on boiling.

Orthophosphoric acid is a tribasic acid giving rise to three series of salts: primary orthophosphates, *e.g.*, NaH_2PO_4; secondary orthophosphates, *e.g.*, Na_2HPO_4; and tertiary orthophosphates, *e.g.*, Na_3PO_4. If a solution of orthophosphoric acid is neutralised with sodium hydroxide solution using methyl orange as indicator, the neutral point is reached when the acid is converted into the primary phosphate (1 equivalent of alkali); with phenol phthalein as indicator, the solution will react neutral when the secondary phosphate is formed (2 equivalents of alkali); with 3 equivalents of alkali, the tertiary or normal phosphate is formed. NaH_2PO_4 is neutral to methyl orange and acid to phenol phthalein, Na_2HPO_4 is neutral to phenol phthalein and alkaline to methyl orange, Na_3PO_4 is alkaline to all indicators because of its extended hydrolysis. Ordinary "sodium phosphate" is disodium hydrogen phosphate, $Na_2HPO_4,12H_2O$.

Solubility.—The phosphates of the alkali metals, with the exception of lithium, and of ammonium are soluble in water; the primary phosphates of the alkaline earth metals are also soluble. All the phosphates of the other metals, and also the secondary and tertiary phosphates of the alkaline earth metals, are sparingly soluble or insoluble in water.

Use disodium hydrogen phosphate, $Na_2HPO_4,12H_2O$.

1. **Silver Nitrate Solution**: yellow precipitate of normal silver orthophosphate Ag_3PO_4 (distinction from meta- and pyro-phosphate), soluble in ammonium hydroxide solution and in dilute nitric acid.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3;$$
$$Na_2HPO_4 + HNO_3 = NaH_2PO_4 + NaNO_3;$$
$$\overline{2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3 + NaH_2PO_4.}$$

2. **Barium Chloride Solution**: white, amorphous precipitate of secondary barium phosphate $BaHPO_4$ from neutral solutions, soluble in dilute mineral acids and in acetic acid. In the presence of ammonium hydroxide solution, the less soluble tertiary phosphate $Ba_3(PO_4)_2$ is precipitated.

$$BaCl_2 + Na_2HPO_4 = BaHPO_4 + 2NaCl.$$
$$2Na_2HPO_4 + 3BaCl_2 + 2NH_4OH$$
$$= Ba_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O.$$

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* These are often referred to simply as phosphates.

3. **Magnesia Mixture** (a solution containing $MgCl_2$, NH_4Cl and NH_4OH) : white, crystalline precipitate of magnesium ammonium phosphate $Mg(NH_4)PO_4,6H_2O$, soluble in acetic acid and in mineral acids, but practically insoluble in 2·5% ammonium hydroxide solution (see under Magnesium, Section **III, 33,** reaction *5*; also under Arsenic, Section **III, 12,** reaction *3*).

$$Na_2HPO_4 + MgCl_2 + NH_4OH = Mg(NH_4)PO_4 + 2NaCl + H_2O.$$

Arsenates also give a similar precipitate with magnesia mixture. They are most simply distinguished from one another by treating the precipitate with silver nitrate solution ; the phosphate turns yellow, whilst the arsenate assumes a chocolate-brown colour.

4. **Ammonium Molybdate Reagent.**—The addition of a large excess (5–10 c.c.) of this reagent to a small volume (0·5–1 c.c.) of a phosphate solution produces a yellow, crystalline precipitate of ammonium phosphomolybdate, to which the formula $(NH_4)_3PO_4,12MoO_3$ was formerly assigned. The correct formula is $(NH_4)_3[PMo_{12}O_{40}]$ or $(NH_4)_3[PO_4(Mo_{12}O_{36})]$. The resultant solution should be strongly acid with nitric acid ; the latter is usually present in the reagent and addition is therefore unnecessary. Precipitation is accelerated by warming to a temperature not exceeding 40°, and by the addition of ammonium nitrate solution. The precipitate is soluble in excess of phosphoric acid or of alkali acid phosphates, and also in solutions of ammonium and alkali hydroxides.

Arsenates give a similar reaction on *boiling* (see under Arsenic, Section **III, 12,** reaction *4*). Ammonium phosphomolybdate dissolves on boiling with ammonium acetate solution, whilst ammonium arseno-molybdate yields a white precipitate on cooling.

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = (NH_4)_3[PMo_{12}O_{40}] + 2NaNO_3 + 21NH_4NO_3 + 12H_2O.$$

Note : Commercial ammonium molybdate has the formula $(NH_4)_6Mo_7O_{24},4H_2O$ (a paramolybdate) and not $(NH_4)_2MoO_4$; the latter formula is employed in the equations for purposes of simplicity, and may exist under the experimental conditions of the reaction.

5. **Ferric Chloride Solution** : yellowish-white precipitate of ferric phosphate $FePO_4$, soluble in dilute mineral acids, but insoluble in dilute acetic acid.

$$Na_2HPO_4 + FeCl_3 \rightleftharpoons FePO_4 + 2NaCl + HCl.$$

Precipitation is incomplete owing to the free mineral acid produced. If the hydrogen ions, arising from the complete ionisation of the mineral acid, are removed by the addition of the salt of a weak acid, such as ammonium or sodium acetate which give rise to the feebly dissociated acetic acid, then precipitation is almost complete. The presence of a large excess of sodium or ammonium acetate reduces the ionisation of the acetic acid still further as a result of the common ion effect (Sect. **I, 14**). This is the basis of one of the methods for the removal of phosphates, which interfere with the precipitation of Group IIIA metals, in qualitative analysis. The solution, in the minimum quantity of dilute hydrochloric acid, is treated with an excess of sodium or ammonium acetate solution, ferric chloride solution is then added drop by drop until the supernatant liquid above the yellowish-white precipitate of ferric phosphate is just coloured distinctly reddish-brown, indicating the presence of excess of ferric ions. On dilution and boiling, the ferric acetate is precipitated as the insoluble basic ferric acetate $Fe(OH)_2.C_2H_3O_2$, which should be filtered hot. The ferric phosphate is appreciably soluble in ferric acetate solution, hence the boiling and the subsequent filtration whilst hot is of great importance for the complete elimination of phosphates (see Section **VI, 2**).

$$FeCl_3 + Na_2HPO_4 + Na.C_2H_3O_2 = FePO_4 + 3\,NaCl + H.C_2H_3O_2.$$

6. **"Meta-stannic Acid" Test.**—The addition of metallic tin to a nitric acid solution of a phosphate, results in the usual conversion of the former into the so-called meta-stannic acid (see under Tin, p. 142), which combines with all the phosphoric acid (provided sufficient tin has been employed) to form an insoluble adsorption compound. This provides the basis of another method for the removal of phosphoric acid from solution, and possesses the advantage that no cations are introduced (see Section **VI, 2**).

7. **Cobalt Nitrate Test.**—Phosphates when heated on charcoal and then moistened with a few drops of cobalt nitrate solution, give a blue mass of the phosphate $NaCoPO_4$. This must not be confused with the blue mass produced with aluminium compounds (see Section **III, 21**).

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O\,;$$
$$NaPO_3 + CoO = NaCoPO_4.$$

8. **Magnesium.**—The only simple method for reducing the stable phosphates consists in heating with magnesium powder, whereby a phosphide is produced. The latter is readily identified by the odour and the inflammability of the phosphine formed on the addition of water. Intimately mix a small quantity of sodium phosphate with magnesium powder and heat in an ignition tube. Moisten the cold mass with water and observe the unpleasant odour of phosphine.

$$Na_3PO_4 + 4Mg = 4MgO + Na_3P\,;$$
$$Na_3P + 3H_2O = PH_3 + 3NaOH.$$

† *9.* **Ammonium Molybdate-Benzidine Test.**—In this test use is made of the fact that benzidine, which is unaffected by normal molybdates and by free molybdic acid, is oxidised in acetic acid solution by phosphomolybdic acid or by its insoluble ammonium salt (see reaction *4* above). This reaction is extremely sensitive ; two coloured products are formed, *viz.*, the blue reduction product of molybdenum compounds (" molybdenum blue ") and the blue oxidation product of benzidine (" benzidine blue "). Moreover, solutions of phosphates which are too dilute to show a visible precipitate with the ammonium molybdate reagent will react with the molybdate reagent and benzidine to give a blue colouration.

Arsenates and silicates with ammonium molybdate yield the ammonium salts of arseno-molybdic $\{H_3[AsMo_{12}O_{40}]\}$ and silico-molybdic $\{H_4[SiMo_{12}O_{40}]\}$ acids respectively ; these complex acids and their salts react similarly with benzidine. However, phosphates may be detected in the presence of arsenates and silicates by preventing the formation of the corresponding molybdo-acids by the use of a tartaric acid-ammonium molybdate reagent which does not react with arsenic and silicic acids but does react with phosphoric acid when the reaction is carried out on filter paper.

Place a drop of the acid solution under test upon quantitative filter paper, add a drop of the molybdate reagent, followed by a drop of the benzidine reagent. Hold the paper over ammonia vapour. A blue stain is formed when most of the mineral acid has been neutralised.

Sensitivity : 1·25 μg. P_2O_5. Concentration limit : 1 in 40,000.

The ammonium molybdate and the benzidine reagent are prepared as described under Silicates, Section **IV, 26,** reaction *7*.

In the **presence of silicates and/or arsenates,** proceed as follows. Place a drop of the test solution upon quantitative filter paper, followed by a drop of the tartaric acid—ammonium molybdate reagent. Hold the paper over a hot wire gauze (or over a sheet of asbestos heated on a hot plate) to accelerate the reaction. Then add a drop of the benzidine reagent and develop over ammonia vapour. A blue colouration results.

Sensitivity : 1·5 μg. P_2O_5 in the presence of 500 times the amount of SiO_2. Concentration limit : 1 in 50,000.

The **tartaric acid-ammonium molybdate reagent** is prepared by dissolving 15 g. of crystallised tartaric acid in 100 c.c. of the ammonium molybdate reagent referred to above.

IV, 29.**REACTIONS OF PYROPHOSPHATES, $P_2O_7^{----}$ AND OF METAPHOSPHATES, PO_3^-

The sodium salts are readily prepared by the ignition of ordinary sodium phosphate and of microcosmic salt respectively :

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O ;$$
$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O.$$

Pyro- and meta-phosphates give the ammonium molybdate test on warming for some time ; this is doubtless due to their initial conversion in solution into orthophosphates. The chief differences between ortho-, pyro- and metaphosphates are incorporated in the following table. The student should carry out all the tests.

Reactions of Ortho-, Pyro- and Meta-phosphates

Reagent	*Orthophosphate*	*Pyrophosphate*	*Metaphosphate*
Silver nitrate solution.	Yellow ppt., soluble in HNO_3 and NH_4OH solution.	White ppt., soluble in HNO_3 and NH_4OH solution.	White ppt. (separates slowly), soluble in HNO_3 and NH_4OH solution.
Albumin and dilute acetic acid.	No coagulation.	No coagulation.	Coagulation.
Barium chloride solution.	White ppt., soluble in dilute acetic acid.	White ppt., insoluble in dilute acetic acid.	No ppt.
Copper sulphate solution.	Pale-blue ppt.	Very pale-blue ppt.	No ppt.
Magnesia mixture.	White ppt., insoluble in excess of the reagent.	White ppt., soluble in excess of reagent, but reprecipitated on boiling.	No ppt., even on boiling.
Cadmium chloride and dilute acetic acid.	No ppt.	White ppt.	No ppt.

IV, 30. **REACTIONS OF PHOSPHITES, HPO_3^{--}

Solubility.—The phosphites of the alkali metals are soluble in water; all other metallic phosphites are insoluble in water.

Use sodium phosphite, $Na_2HPO_3,5H_2O$.

1. **Silver Nitrate Solution**: white precipitate of silver phosphite Ag_2HPO_3, which soon passes in the cold into black metallic silver. Warming is necessary with dilute solutions.

$$Na_2HPO_3 + 2AgNO_3 = Ag_2HPO_3 + 2NaNO_3;$$
$$Ag_2HPO_3 + H_2O = 2Ag + H_3PO_4.$$

2. **Barium Chloride Solution**: white precipitate of barium phosphite $BaHPO_3$, soluble in dilute acids.

3. **Mercuric Chloride Solution**: white precipitate of calomel in the cold; on warming with excess of the phosphite solution, grey metallic mercury is produced.

$$Na_2HPO_3 + 2HgCl_2 + H_2O = H_3PO_4 + Hg_2Cl_2 + 2NaCl;$$
$$Hg_2Cl_2 + Na_2HPO_3 + H_2O = H_3PO_4 + 2Hg + 2NaCl.$$

4. **Potassium Permanganate Solution**; no action in the cold with a solution acidified with acetic acid, but decolourised on warming.

5. **Concentrated Sulphuric Acid**: no reaction in the cold with the solid salt, but on warming sulphur dioxide is evolved.

$$H_3PO_3 + H_2SO_4 = SO_2 + H_3PO_4 + H_2O.$$

6. **Zinc and Dilute Sulphuric Acid.**—Phosphites are reduced by the nascent hydrogen to phosphine PH_3, which may be identified as described in the Gutzeit test under Arsenic (Section **IV, 13**); the silver nitrate paper is stained first yellow and then black.

$$H_3PO_3 + 3Zn + 3H_2SO_4 = PH_3 + 3ZnSO_4 + 3H_2O;$$

$$PH_3 + 6AgNO_3 = PAg_3,3AgNO_3(\text{yellow}) + 3HNO_3;$$

$$PAg_3,3AgNO_3 + 3H_2O = 6Ag(\text{black}) + 3HNO_3 + H_3PO_3.$$

7. **Copper Sulphate Solution**: light blue precipitate of copper phosphite $CuHPO_3$; the precipitate merely dissolves when it is boiled with acetic acid (compare Hypophosphites, Section **IV, 31**).

$$CuSO_4 + Na_2HPO_3 = CuHPO_3 + Na_2SO_4.$$

8. **Action of heat:** inflammable phosphine is evolved, and a mixture of phosphates is produced.

$$8Na_2HPO_3 = 2PH_3 + 4Na_3PO_4 + Na_4P_2O_7 + H_2O.$$

IV, 31. **REACTIONS OF HYPOPHOSPHITES, $H_2PO_2^-$

Solubility.—All hypophosphites are soluble in water.

Use sodium hypophosphite, NaH_2PO_2,H_2O.

1. **Silver Nitrate Solution**: white precipitate of silver hypophosphite AgH_2PO_2, which is slowly reduced to silver at the ordinary temperature, but more rapidly on warming, hydrogen being simultaneously evolved.

$$NaH_2PO_2 + AgNO_3 = AgH_2PO_2 + NaNO_3:$$

$$2AgH_2PO_2 + 4H_2O = 2Ag + 2H_3PO_4 + 3H_2.$$

2. **Barium Chloride Solution**; no precipitate.

3. **Mercuric Chloride Solution**; white precipitate of calomel in the cold, converted by warming into grey, metallic mercury.

$$NaH_2PO_2 + 4HgCl_2 + 2H_2O$$
$$= 2Hg_2Cl_2 + H_3PO_4 + 3HCl + NaCl;$$

$$NaH_2PO_2 + 2HgCl_2 + 2H_2O$$
$$= 2Hg + H_3PO_4 + 3HCl + NaCl.$$

4. **Copper Sulphate Solution** : no precipitate in the cold, but on warming red cuprous hydride Cu_2H_2 is precipitated. The latter evolves hydrogen on treatment with concentrated hydrochloric acid.

$$3H_3PO_2 + 4CuSO_4 + 6H_2O = 2Cu_2H_2 + 3H_3PO_4 + 4H_2SO_4 \,;$$

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

5. **Potassium Permanganate Solution** : reduced immediately in the cold.

6. **Concentrated Sulphuric Acid** : reduced to sulphur dioxide by the solid salt, only on warming.

7. **Concentrated Sodium Hydroxide Solution** : hydrogen is evolved, and a phosphate is produced on warming.

$$NaH_2PO_2 + 2NaOH = 2H_2 + Na_3PO_4.$$

8. **Zinc and Dilute Sulphuric Acid** : inflammable phosphine is evolved (see under Phosphites, Section **IV, 30,** reaction *6*).

9. **Action of Heat** : phosphine is evolved, and a pyrophosphate is produced

$$4NaH_2PO_2 = Na_4P_2O_7 + 2PH_3 + H_2O.$$

IV, 32. REACTIONS OF ARSENITES, AsO_3^{---} AND OF ARSENATES, AsO_4^{---}

See under Arsenic, Sections **III, 11** and **III, 12.**

IV, 33. REACTIONS OF CHROMATES, CrO_4^{--} (AND DICHROMATES, $Cr_2O_7^{--}$)

The metallic chromates are usually coloured solids, yielding yellow solutions when soluble in water. In the presence of dilute mineral acids, *i.e.*, of hydrogen ions, chromates are converted into dichromates ; the latter yield orange-red aqueous solutions. The change is reversed by alkalis, *i.e.*, by hydroxyl ions.

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + H_2O + 2KCl \,;$$

or $$2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O.$$

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O \,;$$

or $$Cr_2O_7^{--} + 2OH^- \rightarrow 2\,CrO_4^- + H_2O.$$

The reactions may also be expressed :

$$2CrO_4^{--} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{--} + H_2O.$$

Solubility.—The chromates of the alkali metals and of calcium and magnesium are soluble in water ; strontium chromate is sparingly soluble. Most other metallic chromates are insoluble in water. Sodium, potassium and ammonium dichromates are soluble in water.

Use potassium chromate, K_2CrO_4, or potassium dichromate, $K_2Cr_2O_7$.

1. **Barium Chloride Solution** : pale yellow precipitate of barium chromate $BaCrO_4$, insoluble in water and in acetic acid, but soluble in dilute mineral acids (for explanation, see Section **I, 17.**

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2KCl.$$

2. **Silver Nitrate Solution** : brownish-red precipitate of silver chromate Ag_2CrO_4 with a solution of a chromate. The precipitate is soluble in dilute nitric acid and in ammonium hydroxide solution, but is insoluble in acetic acid.

A reddish-brown precipitate of silver dichromate $Ag_2Cr_2O_7$ is formed with a concentrated solution of a dichromate ; this passes, on boiling with water, into the less soluble silver chromate.

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3 ;$$
$$K_2Cr_2O_7 + 2AgNO_3 = Ag_2Cr_2O_7 + 2KNO_3 ;$$
$$2Ag_2Cr_2O_7 + H_2O = 2Ag_2CrO_4 + H_2Cr_2O_7.$$

3. **Lead Acetate Solution** : yellow precipitate of lead chromate $PbCrO_4$, insoluble in acetic acid, but soluble in dilute nitric acid.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2K.C_2H_3O_2.$$

The precipitate is soluble in sodium hydroxide solution ; acetic acid reprecipitates the chromate from the latter solution.

The solubility in sodium hydroxide solution is due to the formation of the soluble complex salt, sodium plumbite $Na_2[PbO_2]$, which reduces the Pb^{++} ion concentration to such an extent that the solubility product of lead chromate is no longer exceeded, and consequently the latter dissolves (compare Section **I, 17**).

$$PbCrO_4 + 4NaOH = Na_2[PbO_2] + Na_2CrO_4 + 2H_2O.$$

4. **Hydrogen Peroxide.**—If an acid solution of a chromate is treated with hydrogen peroxide, a deep-blue solution of the so-called *perchromic acid*, variously formulated as $HCrO_5$, H_3CrO_7, H_3CrO_8 and H_7CrO_{10}, is obtained. The blue solution is very unstable, and soon decomposes, yielding oxygen and a green solution of a chromic salt. The blue compound is soluble in ether, amyl alcohol or ethyl acetate, and can be readily extracted from aqueous solution by these solvents ; it is more stable when dissolved in these solvents. Just acidify a cold solution of a chromate with dilute sulphuric acid, add **2–3** c.c. of ether (*highly inflammable*)[‡], then **2–3** c.c. of 10 volume hydrogen peroxide and shake; the ethereal solution is coloured blue. The perchromic acid is more stable below 0° than at the laboratory temperature.

$$H_2Cr_2O_7 + 7H_2O_2 = 2H_3CrO_8 + 5H_2O\,;$$
$$2H_3CrO_8 + 3H_2SO_4 = Cr_2(SO_4)_3 + 5O_2 + 6H_2O.$$

5. **Hydrogen Sulphide.**—An acid solution of a chromate is reduced by this reagent to a green solution of a chromic salt, accompanied by the separation of sulphur[*].

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + 2KCl + H_2O\,;$$
$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = Cr_2(SO_4)_3 + 3S + K_2SO_4 + 7H_2O.$$

6. **Sulphur Dioxide**: in the presence of dilute mineral acid, a green chromic salt is produced.

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O.$$
$$K_2Cr_2O_7 + 3H_2SO_3 + 8HCl = 2CrCl_3 + 2KCl + 3H_2SO_4 + 4H_2O.$$

Chromates in acid solution, or dichromates, are similarly reduced to green chromic salts by potassium iodide, ferrous sulphate and ethyl alcohol.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + 3I_2 + 4K_2SO_4 + 7H_2O.$$
$$K_2Cr_2O_7 + 6FeSO_4 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O.$$
$$K_2Cr_2O_7 + 3C_2H_5.OH + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O + 3CH_3.CHO \text{ (acetaldehyde)}.$$

7. **Concentrated Hydrochloric Acid.**—On heating a solid chromate or dichromate with concentrated hydrochloric acid,

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[‡] A blank test must be performed with the ether alone (see Section **IV, 43,** reaction *1*).

[*] In qualitative analysis, the production of sulphur in the reduction of dichromates by hydrogen sulphide is sometimes troublesome. This can be avoided (*a*) by heating the solid substance with concentrated hydrochloric acid, evaporating off most of the acid and then diluting with water, or (*b*) by warming with hydrochloric acid and alcohol or 10% formaldehyde solution. The use of sulphur dioxide is not recommended as sulphuric acid is formed, and this will precipitate lead, strontium and barium, if these metals are present.

$$K_2Cr_2O_7 + 8HCl + 3H.CHO = 2CrCl_3 + 2KCl + 3\,H.CO_2H + 4H_2O$$
$$K_2Cr_2O_7 + 8HCl + 3C_2H_5.OH = 2CrCl_3 + 2KCl + 3CH_3.CHO + 7H_2O.$$

chlorine is evolved, and a solution of chromic chloride is produced.

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O.$$

8. **Concentrated Sulphuric Acid and a Chloride.**—See chromyl chloride test under Chlorides, Section **IV, 14**, reaction *5*).

9. **α-Naphthylamine.**—If a trace of the solid reagent is added to a solution of a chromate or dichromate and then tartaric acid added, a blue colour is produced.

10. **Diphenylcarbazide Reagent.**—The solution is acidified with dilute sulphuric acid or with dilute acetic acid, and 1–2 c.c. of the reagent added. A deep red colouration is produced. With small quantities of chromates, the solution is coloured violet. This test is very much more sensitive than the hydrogen peroxide-ether reaction *4*.

Full details of the use of the reagent as a spot test are given under Chromium, Section **III, 22**, reaction *7*.

IV, 34. **REACTIONS OF PERMANGANATES, MnO_4^-

Solubility.—All permanganates are soluble in water forming purple (reddish-violet) solutions.

Use potassium permanganate, $KMnO_4$.

1. **Hydrogen Peroxide.**—The addition of this reagent to a solution of potassium permanganate, acidified with dilute sulphuric acid, results in decolourisation and the evolution of pure but moist oxygen.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O.$$

2. **Hydrogen Sulphide** in the presence of dilute sulphuric acid, the purple colour of the solution is discharged and sulphur is precipitated.*

$$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O.$$

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* To avoid the production of sulphur by the reduction of potassium permanganate by hydrogen sulphide in systematic qualitative analysis, the solution may be reduced with formaldehyde solution, or the solid substance may be boiled with concentrated hydrochloric acid. The use of sulphur dioxide is not recommended (see footnote in connexion with Chromates, Sect. **IV, 33**, reaction *5*).

$$2KMnO_4 + 6HCl + 5H.CHO = 2MnCl_2 + 2KCl + 5H.CO_2H + 3H_2O.$$

Similar results are obtained with other reducing agents in the presence of dilute sulphuric acid. These include sulphur dioxide, ferrous sulphate, potassium iodide, sodium nitrite and oxalic acid ; in the last case, the reaction proceeds best at about 60°.

$$2KMnO_4 + 5SO_2 + 2H_2O = 2MnSO_4 + K_2SO_4 + 2H_2SO_4.‡$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

$$2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 5I_2 + 8H_2O.$$

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5HNO_3 + 3H_2O.$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

In *alkaline* solution, the permanganate is decolourised, but manganese dioxide is precipitated. In the presence of sodium hydroxide solution, potassium iodide is converted into potassium iodate, and sodium sulphite solution into sodium sulphate on boiling.

$$2KMnO_4 + KI + H_2O = KIO_3 + 2MnO_2 + 2KOH.$$

$$2KMnO_4 + 3Na_2SO_3 + H_2O = 3Na_2SO_4 + 2MnO_2 + 2KOH.$$

3. **Concentrated Hydrochloric Acid.**—All permanganates on boiling with concentrated hydrochloric acid evolve chlorine.

$$2KMnO_4 + 16HCl = 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O.$$

4. **Concentrated Sulphuric Acid.**—Permanganates dissolve in this reagent to yield a green solution, which contains manganese heptoxide (permanganic anhydride) Mn_2O_7 ; the solution is liable to explode spontaneously at the ordinary temperature, and a very vigorous explosion may result on warming. The student is therefore warned not to carry out this experiment except with minute quantities of materials (not more than 0·1 gram) and in the latter case under the direct supervision of the teacher. The experiment is best omitted.

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‡ Some dithionic acid $H_2S_2O_6$ may be formed in this reaction, the quantity being dependent upon the experimental conditions.

$$2KMnO_4 + 6SO_2 + 2H_2O = 2MnSO_4 + 2KHSO_4 + H_2S_2O_6$$

On warming potassium permanganate with ***dilute*** sulphuric acid, oxygen is evolved.

$$2KMnO_4 + H_2SO_4 \text{ (conc.)} = Mn_2O_7 + K_2SO_4 + H_2O.$$

$$4KMnO_4 + 4H_2SO_4 = 4MnO_2 + 4KHSO_4 + 3O_2 + 2H_2O.$$

5. **Potassium Hydroxide Solution.**—On warming a concentrated solution of potassium permanganate with concentrated potassium hydroxide solution, a green solution of *potassium manganate* is produced and oxygen is evolved. When the manganate solution is poured into a large volume of water or is acidified with dilute sulphuric acid, the purple colour of the potassium permanganate is restored.

$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2.$$

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

A manganate is produced when a manganese compound is fused with potassium nitrate and sodium carbonate (see Section **III, 26**).

6. **Action of Heat.**—When potassium permanganate is heated in a test-tube, pure oxygen is evolved, and a black residue of potassium manganate K_2MnO_4 and manganese dioxide remains behind. On extracting with a little water and filtering, a green solution of potassium manganate is obtained.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

IV, 35. **REACTIONS OF ACETATES, $C_2H_3O_2^-$

Solubility.—All normal acetates, with the exception of silver and mercurous acetates which are sparingly soluble, are readily soluble in water. Some basic acetates, *e.g.*, those of iron, aluminium and chromium, are insoluble in water. The free acid, $CH_3.CO_2H$ or $H.C_2H_3O_2$, is a colourless liquid with a pungent odour, boiling point 117°, melting point 17°, and is miscible with water in all proportions ; it has a corrosive action on the skin.

Use sodium acetate, $Na.C_2H_3O_2,3H_2O$ (or $CH_3.CO_2Na,3H_2O$).

1. **Dilute Sulphuric Acid** : acetic acid, easily recognised by its vinegar-like odour, is evolved on warming.

$$Na.C_2H_3O_2 + H_2SO_4 = NaHSO_4 + H.C_2H_3O_2.$$

2. **Concentrated Sulphuric Acid** : acetic acid is evolved on heating, together with sulphur dioxide, the latter tending to mask the penetrating odour of the concentrated acetic acid vapour. The test with dilute sulphuric acid, in which the acetic acid vapour is diluted with steam, is therefore to be preferred as a test for an acetate.

3. **Ethyl Alcohol and Concentrated Sulphuric Acid.**—One gram of the solid acetate is treated with 1 c.c. of concentrated sulphuric acid and 2–3 c.c. of rectified spirit in a test-tube, and the whole gently warmed for several minutes; ethyl acetate $C_2H_5.C_2H_3O_2$ is formed, which is recognised by its pleasant, fruity odour. On cooling and dilution with water on a clock glass, the fragrant odour will be more readily detected.

$C_2H_5.OH + H.C_2H_3O_2 \rightleftharpoons C_2H_5.C_2H_3O_2 + H_2O$ (the sulphuric acid acts as a dehydrating agent).

It is preferable to use *iso*-amyl alcohol because the odour of the resulting *iso*-amyl acetate is more readily distinguished from the alcohol itself than is the case with ethyl alcohol. It is well to run a parallel test with a known acetate and to compare the odours of the two products.

4. **Silver Nitrate Solution**: a white, crystalline precipitate of silver acetate $Ag.C_2H_3O_2$ is produced in concentrated solutions in the cold. The precipitate is more soluble in boiling water (10·4 g. per litre at 20° and 25·2 g. per litre at 80°) and readily soluble in ammonium hydroxide solution.

$$Na.C_2H_3O_2 + AgNO_3 = Ag.C_2H_3O_2 + NaNO_3.$$

5. **Barium, Calcium or Mercuric Chloride Solution**: no precipitate.

6. **Ferric Chloride Solution**: deep-red colouration, due to ferric acetate $Fe(C_2H_3O_2)_3$, is produced with neutral solutions of acetates. On diluting and boiling the red solution, the iron is precipitated as basic ferric acetate $Fe(OH)_2.C_2H_3O_2$. The colouration is destroyed by dilute hydrochloric acid.

$$FeCl_3 + 3Na.C_2H_3O_2 = Fe(C_2H_3O_2)_3 + 3NaCl;$$
$$Fe(C_2H_3O_2)_3 + 2H_2O = Fe(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

7. **Cacodyl Oxide Reaction.**—If a dry acetate, preferably that of sodium or potassium, is heated in an ignition tube or test-tube with a small quantity of arsenious oxide, an extremely nauseating odour of cacodyl oxide is produced. All cacodyl compounds are *extremely* poisonous; the experiment must therefore be performed on a very small scale, and preferably in the fume chamber. Mix not more than 0·5 gram of sodium acetate with 0·5 gram of arsenious oxide in an ignition tube and warm; observe the extremely unpleasant odour that is produced.

$$4Na.C_2H_3O_2 + As_2O_3 = (CH_3)_2As.O.As(CH_3)_2 + 2Na_2CO_3 + 2CO_2.$$

8. **Lanthanum Nitrate Test.**—Treat 0·5 c.c. of the acetate solution with 0·5 c.c. of a 5% lanthanum nitrate solution, add 0·5 c.c. of iodine solution and a few drops of ammonium hydroxide solution, and heat slowly to the boiling point. A blue colour is produced; this is probably due to the adsorption of the iodine by the basic lanthanum acetate. This reaction provides an extremely sensitive test for an acetate.

Sulphates and phosphates interfere, but can be removed by precipitation with barium nitrate solution before applying the test. Propionates give a similar reaction.

† The spot-test technique is as follows. Mix a drop of the test solution on a spot plate with a drop of 5 per cent lanthanum nitrate solution and a drop of 0·01*N*-iodine. Add a drop of *N*-ammonium hydroxide solution. Within a few minutes a blue to blue-brown ring will develop round the drop of ammonia solution.

Sensitivity: 50 μg. $H.C_2H_3O_2$. Concentration limit: 1 in 2,000.

† *9.* **Formation of Indigo Test.**—The test depends upon the conversion of acetone, formed by the dry distillation of acetates (see reaction *10*), into indigo. No other fatty acids give this test, but the sensitivity is reduced in their presence.

Mix the solid test sample with calcium carbonate or, alternatively, evaporate a drop of the test solution to dryness with calcium carbonate; both operations may be carried out in the hard glass tube of Fig. **39**. Cover the open end of the tube with a strip of quantitative filter paper moistened with a freshly-prepared solution of *o*-nitrobenzaldehyde in 2*N*-sodium hydroxide, and hold the paper in position with a small glass cap or a small watch glass. Insert the tube into a hole in an asbestos or "uralite" sheet and heat the tube gently. Acetone is evolved which colours the paper blue or bluish-green. For minute amounts of acetates, it is best to remove the filter paper after the reaction and treat it with a drop of dilute hydrochloric acid; the original yellow colour of the paper is thus bleached and the blue colour of the indigo is more readily apparent.

Sensitivity: 60 μg. $H.C_2H_3O_2$.

10. **Action of Heat.**—All acetates decompose upon strong ignition, yielding the highly inflammable acetone $CH_3.CO.CH_3$ and a residue, which consists of the carbonates for the alkali acetates, of the oxides for the acetates of the alkaline earth and heavy metals, and of the metal for the acetates of silver and the noble metals. Carry out the experiment in an ignition tube with sodium acetate and lead acetate.

$$2Na.C_2H_3O_2 = CH_3.CO.CH_3 + Na_2CO_3.$$

IV, 36. **REACTIONS OF FORMATES, $H.CO_2^-$

Solubility.—With the exception of the lead, silver and mercurous salts which are sparingly soluble, most formates are soluble in water. The free acid $H.CO_2H$ is a pungent smelling liquid, boiling point 100·5°, melting point 8°, miscible with water in all proportions, and producing blisters when allowed to come into contact with the skin.

Use sodium formate, $H.CO_2Na$.

1. **Dilute Sulphuric Acid**: formic acid is liberated, the pungent odour of which can be detected on warming the mixture.

$$H.CO_2Na + H_2SO_4 = NaHSO_4 + H.CO_2H.$$

2. **Concentrated Sulphuric Acid**: carbon monoxide (*highly poisonous*) is evolved on warming; the gas should be ignited and the characteristic blue flame obtained.

$$H.CO_2Na + H_2SO_4 = CO + NaHSO_4 + H_2O.$$

3. **Ethyl Alcohol and Concentrated Sulphuric Acid**: a pleasant odour, due to ethyl formate $H.CO_2C_2H_5$, is apparent on warming (for details, see under Acetates, Section **IV, 35,** reaction *3*).

$$H.CO_2Na + C_2H_5OH \rightleftharpoons H.CO_2C_2H_5 + H_2O.$$

4. **Silver Nitrate Solution**: white precipitate of silver formate $H.CO_2Ag$ in neutral solutions, slowly reduced at the ordinary temperature and more rapidly on warming, a black precipitate of silver being formed (distinction from acetate). With very dilute solutions, the silver may be deposited in the form of a mirror on the walls of the tube.

$$H.CO_2Na + AgNO_3 = H.CO_2Ag + NaNO_3;$$
$$2H.CO_2Ag = 2Ag + H.CO_2H + CO_2.$$

5. **Barium or Calcium Chloride Solution**: no precipitate.

6. **Ferric Chloride Solution**: a red colouration, due to ferric formate $Fe(H.CO_2)_3$, is produced in neutral solutions; the colour is discharged by hydrochloric acid. If the red solution is diluted and boiled, a brown basic ferric formate $(H.CO_2)Fe(OH)_2$ is precipitated.

$$3H.CO_2Na + FeCl_3 = Fe(H.CO_2)_3 + 3NaCl;$$
$$Fe(H.CO_2)_3 + 2H_2O = (H.CO_2)Fe(OH)_2 + 2H.CO_2H.$$

7. **Mercuric Chloride Solution**: white precipitate of mercurous chloride Hg_2Cl_2 is produced on warming ; this passes into grey, metallic mercury in presence of excess of the formate solution (distinction from acetate).

$$2H.CO_2Na + 2HgCl_2 = Hg_2Cl_2 + 2NaCl + CO + CO_2 + H_2O ;$$
$$2H.CO_2Na + Hg_2Cl_2 = 2Hg + 2NaCl + CO + CO_2 + H_2O.$$

8. **Mercuric Formate Test.**—Free formic acid is necessary for this test. The solution of the formate is acidified with dilute sulphuric acid and shaken vigorously with a little mercuric oxide ; it is then filtered from the undissolved oxide. The filtrate, which contains mercuric formate $(H.CO_2)_2Hg$, on boiling gives momentarily a white precipitate of mercurous formate $(H.CO_2)_2Hg_2$, which rapidly changes to a grey precipitate of metallic mercury.

$$2H.CO_2H + HgO = (H.CO_2)_2Hg + H_2O ;$$
$$2(H.CO_2)_2Hg = (H.CO_2)_2Hg_2 + H.CO_2H + CO_2 ;$$
$$(H.CO_2)_2Hg_2 = 2Hg + H.CO_2H + CO_2.$$

9. **Action of Heat.**—Cautious ignition of the formates of the alkali metals yields the corresponding oxalates (for tests, see Section **IV, 37**) and hydrogen.

$$2H.CO_2Na = Na_2.C_2O_4 + H_2.$$

IV, 37. **REACTIONS OF OXALATES, $C_2O_4^{--}$

Solubility.—The oxalates of the alkali metals and of ferrous iron are soluble in water ; all other oxalates are either insoluble or sparingly soluble in water. They are all soluble in dilute acids :

$$Ca.C_2O_4 + 2HCl = H_2.C_2O_4 + 2HCl.$$

Some of the oxalates dissolve in a concentrated solution of oxalic acid by virtue of the formation of soluble acid or complex oxalates. Oxalic acid (a dibasic acid) is a colourless, crystalline solid $H_2C_2O_4,2H_2O$ (or $HO_2C.CO_2H,2H_2O$), and becomes anhydrous on heating to 110° ; it is readily soluble in water (111 g. per litre at 20°).

Use sodium oxalate, $Na_2.C_2O_4$, or ammonium oxalate, $(NH_4)_2.C_2O_4,H_2O$.

1. **Concentrated Sulphuric Acid** : decomposition of all solid oxalates occurs with the evolution of carbon monoxide and carbon dioxide ; the latter can be detected by passing the escaping gases through lime-water (distinction from formate) and the former by burning it at the mouth of the tube. With dilute sulphuric acid, there is no visible action ; in the presence of manganese dioxide, however, carbon dioxide is evolved.

$H_2.C_2O_4 + H_2SO_4 = CO + CO_2 + H_2O + H_2SO_4$ (the sulphuric acid acts as a dehydrating agent).

2. **Silver Nitrate Solution**: white, curdy precipitate of silver oxalate $Ag_2.C_2O_4$, sparingly soluble in water, soluble in ammonium hydroxide solution and in dilute nitric acid.

$$(NH_4)_2.C_2O_4 + 2AgNO_3 = Ag_2.C_2O_4 + 2NH_4NO_3.$$

3. **Calcium Chloride Solution**: white, crystalline precipitate of calcium oxalate $Ca.C_2O_4$ from neutral solutions, insoluble in dilute acetic acid, oxalic acid and in ammonium oxalate solution, but soluble in dilute hydrochloric acid and in dilute nitric acid. It is the most insoluble of all oxalates (0·0067 g. per litre at 13°) and is even precipitated by calcium sulphate solution and acetic acid. Barium chloride solution similarly gives a white precipitate of barium oxalate $Ba.C_2O_4$, sparingly soluble in water (0·016 g. per litre at 8°), but soluble in solutions of acetic and of oxalic acids.

$$(NH_4)_2.C_2O_4 + CaCl_2 = Ca.C_2O_4 + 2NH_4Cl.$$

4. **Potassium Permanganate Solution**: decolourised when warmed in acid solution to 60°–70°. The bleaching of permanganate solution is also effected by many other organic compounds, but if the evolved carbon dioxide is tested for by the lime water reaction (Section **IV, 2,** reaction *1*), the test becomes specific for oxalates.

$$2KMnO_4 + 3H_2SO_4 + 5H_2.C_2O_4$$
$$= 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

5. **Resorcinol Test.**—Place a few drops of the test solution in a test-tube: add several drops of dilute sulphuric acid and a speck or two of magnesium powder. When the metal has dissolved, add about 0·1 g. of resorcinol, and shake until dissolved. Cool. Carefully pour down the side of the tube 3–4 c.c. of concentrated sulphuric acid. A blue ring will form at the junction of the two liquids. Upon warming the sulphuric acid layer at the bottom of the tube very gently (**CAUTION**), the blue colour spreads downwards from the interface and eventually colours the whole of the sulphuric acid layer.

Citrates do not interfere. In the presence of tartrates, a blue ring is obtained in the cold or upon very gentle warming (compare similar test under Tartrates in the following Section).

6. **Manganous Sulphate Test.**—A solution of manganous sulphate is treated with sodium hydroxide solution, and the resultant mixture warmed gently to convert it into mangano-manganic hydroxide. After cooling, the solution of the oxalate, made acid with dilute sulphuric acid, is added. The precipitate dissolves and a red colour is produced. The latter is probably due to the formation of the complex ion $[Mn(C_2O_4)_3]^{---}$.

7. **Action of Heat.**—All oxalates decompose upon ignition. Those of the alkali metals and of the alkaline earths yield chiefly the carbonates and carbon monoxide; a little carbon is also formed. The oxides of the metals whose carbonates are easily decomposed into stable oxides, are converted into carbon monoxide, carbon dioxide and the oxide, *e.g.*, magnesium and zinc oxalates. Silver oxalate yields silver and carbon dioxide; silver oxide decomposes on heating. Oxalic acid decomposes into carbon dioxide and formic acid, the latter being further partially decomposed into carbon monoxide and water.

$$\begin{aligned} 7Na_2.C_2O_4 &= 7Na_2CO_3 + 3CO + 2CO_2 + 2C\,; \\ Ba.C_2O_4 &= BaCO_3 + CO_2\,; \\ Mg.C_2O_4 &= MgO + CO + CO_2\,; \\ Ag_2.C_2O_4 &= 2Ag + 2CO_2\,; \\ H_2.C_2O_4 &= H.CO_2H + CO_2\,; \\ H.CO_2H &= CO + H_2O. \end{aligned}$$

† *8.* **Formation of Aniline Blue Test.**—Upon heating insoluble oxalates with syrupy phosphoric acid and diphenylamine or upon heating together oxalic acid and diphenylamine, the dyestuff aniline blue (or diphenylamine blue) is formed. Formates, acetates, tartrates, citrates, succinates, benzoates and salts of other organic acids do not react under these experimental conditions. In the presence of other anions which are precipitated by calcium chloride solution, *e.g.*, tartrate, sulphate, sulphite, phosphate and fluoride, it is best to heat the precipitate formed by calcium chloride with phosphoric acid as detailed below.

Place a few milligrams of the test sample (or, alternatively, use the residue obtained by evaporating 2 drops of the test solution to dryness) in a micro test-tube, add a little pure diphenylamine, and melt over a free flame. When cold, take up the melt in a drop or two of alcohol when the latter will be coloured blue.

Sensitivity: 5 μg. $H_2C_2O_4$. Concentration limit: 1 in 10,000.

In the presence of anions which are precipitated by calcium chloride solution, proceed as follows. Precipitate the acetic acid test solution with calcium chloride solution, and collect the precipitate on a filter or in a centrifuge tube. Remove the water from the precipitate either by drying or by washing with alcohol and ether. Mix a small amount of the precipitate with diphenylamine in a dry micro test-tube, add a little syrupy phosphoric acid, and heat gently over a free flame. Calcium phosphate and free oxalic acid are formed, and the latter condenses with the diphenylamine to aniline blue and colours the hot phosphoric acid blue. The colour disappears on cooling. Dissolve the melt in alcohol, when a blue colouration appears. Pour the alcoholic solution into water thus precipitating the excess of diphenylamine, which is coloured light blue by the adsorption of the dyestuff. The dye may be extracted from aqueous solution by ether.

IV, 38. **REACTIONS OF TARTRATES, $C_4H_4O_6^{--}$

Solubility.—Tartaric acid, $HO_2C.CH(OH)\,CH(OH).CO_2H$ or $H_2.C_4H_4O_6$, is a crystalline solid, which is extremely soluble in water; it is a dibasic acid. The potassium and ammonium acid salts are sparingly soluble in water; those of the other alkali metals are readily soluble. The normal tartrates of the alkali metals are easily soluble, those of the other metals being sparingly soluble in water, but dissolve in solutions of alkali tartrates forming complex salts, which often do not give the typical reactions of the metals present.

The most important commercial salts are "tartar emetic" $K(SbO).C_4H_4O_6,0{\cdot}5H_2O$, "Rochelle salt" $KNa.C_4H_4O_6,4H_2O$, and "cream of tartar" $KH.C_4H_4O_6$.

Use Rochelle salt, $KNa.C_4H_4O_6,4H_2O$.

1. **Concentrated Sulphuric Acid.**—When a solid tartrate is heated with concentrated sulphuric acid, it is decomposed in a complex manner. *Charring* occurs almost immediately (owing to the separation of carbon), carbon dioxide and carbon monoxide are evolved, together with some sulphur dioxide; the last-named probably arises from the reduction of the sulphuric acid by the carbon. An empyreumatic odour, reminiscent of burnt sugar, can be detected in the evolved gases. Dilute sulphuric acid has no visible action.

$$H_2.C_4H_4O_6 = CO + CO_2 + 2C + 3H_2O\,;$$
$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O.$$

2. **Silver Nitrate Solution**: white, curdy precipitate of silver tartrate $Ag_2.C_4H_4O_6$ from neutral solutions of tartrates, soluble in excess of the tartrate solution, in dilute ammonium hydroxide solution and in dilute nitric acid. On warming the ammoniacal solution, metallic silver is precipitated; this can be deposited in the form of a mirror under suitable conditions.

The **silver mirror test** is best performed as follows. The solution of the tartrate is acidified with dilute nitric acid, excess of silver nitrate solution added and any precipitate present filtered off. Very dilute ammonium hydroxide solution (approximately $M/50$) is then added to the solution until the precipitate at first formed is *nearly* redissolved, the solution is filtered, and the filtrate collected in a clean test-tube; the latter is then placed in a beaker of boiling water. A brilliant mirror is formed on the sides of the tube after a few minutes. The test-tube may be cleaned either by boiling with chromic acid mixture or by boiling it with a little sodium hydroxide solution, and then rinsing it well with distilled water.

An *alternative method* for carrying out the silver mirror test is the following. Prepare ammoniacal silver nitrate solution by placing 5 c.c. of silver nitrate solution in a thoroughly clean test-tube and add 2–3 drops of dilute sodium hydroxide solution; add dilute ammonia solution dropwise until the precipitated silver oxide is *almost* redissolved (this procedure reduces the danger of the formation of the explosive silver azide AgN_3 to a minimum). Introduce about 0·5 c.c. of the neutral tartrate solution. Place the tube in warm water. A silver mirror is formed in a few minutes.

The reaction is interfered with by other acids. It is best to isolate the potassium hydrogen tartrate, as in reaction *4* below, before carrying out the test.

$$KNa.C_4H_4O_6 + 2AgNO_3 = Ag_2.C_4H_4O_6 + KNO_3 + NaNO_3.$$

3. **Calcium Chloride Solution**: white, crystalline precipitate of calcium tartrate $Ca.C_4H_4O_6$ with a concentrated neutral solution. The precipitate is soluble in dilute acetic acid (difference from oxalate), in dilute mineral acids and in cold alkali solutions. An excess of the reagent must be added because calcium tartrate dissolves in an excess of an alkali tartrate solution forming a complex tartrate ion, $[Ca(C_4H_4O_6)_2]^{--}$. Precipitation is slow in dilute solutions, but may be accelerated by vigorous shaking or by rubbing the glass walls of the test-tube with a glass rod.

$$CaCl_2 + NaK.C_4H_4O_6 = Ca.C_4H_4O_6 + NaCl + KCl.$$

4. **Potassium Chloride Solution.**—When a concentrated, neutral solution of a tartrate is treated with a solution of a potassium salt (*e.g.*, potassium chloride) and then acidified with acetic acid, a colourless crystalline precipitate of potassium hydrogen tartrate $KH.C_4H_4O_6$ is obtained. The precipitate forms slowly in dilute solutions; crystallisation is induced by vigorous shaking or by rubbing the walls of the vessel with a glass rod.

$$KNa.C_4H_4O_6 + KCl + H.C_2H_3O_2 = KH.C_4H_4O_6 + NaCl + K.C_2H_3O_2.$$

5. **Fenton's Test.**—Add 1 drop of a saturated solution of ferrous sulphate to about 5 c.c. of the neutral solution of the tartrate, and then 2–3 drops of hydrogen peroxide solution (10 volume). An intense violet colouration is developed on adding excess of sodium hydroxide solution.

The violet colour is due to the formation of a salt of dihydroxy-maleic acid $CO_2H.C(OH) = C(OH).CO_2H$.

The test is not given by citrates, malates or succinates.

6. **Resorcinol Test.**—Place a few drops of the test solution in a test-tube ; add several drops of dilute sulphuric acid and a speck or two of magnesium powder. When the metal has dissolved, add about 0·1 g. of resorcinol, and shake until dissolved. Cool. Carefully pour down the side of the tube 3–4 c.c. of concentrated sulphuric acid. Upon warming the sulphuric acid layer at the bottom of the tube very gently (**CAUTION**) red layer (or ring) forms at the junction of the two liquids. With continued *gentle* heating, the red colour spread downwards from the interface and eventually colours the whole of the sulphuric acid layer.

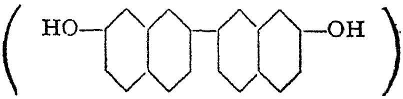
Citrates do not interfere. In the presence of oxalate, a blue ring is formed in the cold and on *gentle* warming of the sulphuric acid layer at the bottom of the tube the blue colouration spreads downwards into the concentrated acid layer and a red ring forms at the interface.

The colour is due to the formation of a condensation product of resorcinol $C_6H_4(OH)_2$ and glycollic aldehyde $CH_2OH.CHO$, the latter arising from the action of the sulphuric acid upon the tartaric acid. The formula of the condensation product is $CH_2OH.CH[C_6H_3(OH)_2]_2$.

7. **Copper Hydroxide Test.**—Tartrates dissolve copper hydroxide in the presence of excess of alkali hydroxide solution to form the dark blue cupri-tartrate ion, which is best detected by filtering the solution. If only small quantities of tartrate are present, the filtrate should be acidified with acetic acid and tested for copper by the potassium ferrocyanide test. Arsenates, ammonium salts, and organic compounds convertible into tartaric acid also give a blue colouration, and should therefore be absent or be removed.

The experimental details are as follows. Treat the test solution with an equal volume of $2N$-sodium or potassium hydroxide (or treat the test solid directly with a few c.c. of the alkali hydroxide solution, warm for a few minutes with stirring, and then cool), add a few drops of copper sulphate solution (*i.e.*, just sufficient to yield a visible precipitate of cupric hydroxide), shake the mixture vigorously for 5 minutes, and filter. If the filtrate is not clear, warm to coagulate the colloidal copper hydroxide, and filter again. A distinct blue colouration indicates the presence of a tartrate. If a pale colouration is obtained, it is advisable to add concentrated ammonia solution dropwise when the blue colour deepens or, better, to acidify with $2N$-acetic acid and add potassium ferrocyanide solution to the clear solution whereupon a reddish-brown precipitate or (with a trace of a tartrate) a red colouration is obtained.

†*8*. **$\beta\beta'$-Dinaphthol Test**.—



When a solution of $\beta\beta'$-dinaphthol in concentrated sulphuric acid is heated with tartaric acid, a green colouration is obtained. Oxalic, citric, succinic and cinnamic acids do not interfere.

Heat a few milligrams of the solid test sample or a drop of the test solution with 1·2 c.c. of the dinaphthol reagent in a water bath at 85°C for 30 minutes. A luminous green fluorescence appears during the heating, which intensifies on cooling, and at the same time the violet fluorescence of the reagent disappears.

Sensitivity : 10μg. tartaric acid. Concentration limit : 1 in 5,000.

The **reagent** consists of a solution of 0·05 g. of $\beta\beta'$-dinaphthol in 100 c.c. of concentrated sulphuric acid.

9. **Action of Heat.**—The tartrates and also tartaric acid decompose in a complex manner on heating ; charring takes place, a smell of burnt sugar is apparent, and inflammable vapours are evolved.

IV, 39. **REACTIONS OF CITRATES, $C_6H_5O_7^{---}$

Solubility.—Citric acid, $HO_2C.CH_2.C(OH)CO_2H.CH_2.CO_2H,H_2O$ or $H_3.C_6H_5O_7,H_2O$, is a crystalline solid which is very soluble in water ; it becomes anhydrous at 55° and melts at 160°. It is a tribasic acid, and therefore gives rise to three series of salts. The normal citrates of the alkali metals dissolve readily in water ; other metallic citrates are sparingly soluble. The acid citrates are more soluble than the acid tartrates.

Use sodium citrate, $Na_3.C_6H_5O_7,2H_2O$.

1. **Concentrated Sulphuric Acid.**—When a solid citrate is heated with concentrated sulphuric acid, carbon monoxide and carbon dioxide are evolved ; the solution *slowly* darkens owing to the separation of carbon, and sulphur dioxide is evolved (compare Tartrates, Section **IV, 30,** which char almost immediately).

The first products of the reaction are carbon monoxide and acetone dicarboxylic acid (I) ; the latter undergoes further partial decomposition into acetone (II) and carbon dioxide.

$$HO_2C.CH_2.C(OH)CO_2H.CH_2.CO_2H = CO + H_2O + HO_2C.CH_2.CO.CH_2.CO_2H \text{ (I)};$$

$$HO_2C.CH_2.CO.CH_2.CO_2H = CH_3.CO.CH_3 \text{ (II)} + 2CO_2.$$

Use may be made of the intermediate formation of acetone dicarboxylic acid and of the interaction of the latter with sodium nitroprusside solution to yield a red colouration as a test for citrates. When about 0·5 g. of a citrate or of citric acid is treated with 1 c.c. of concentrated sulphuric acid for 1 minute, the mixture cooled, cautiously diluted with water, rendered alkaline with sodium hydroxide solution, and then a few c.c. of a freshly-prepared solution of sodium nitroprusside added, an intense red colouration results.

2. **Silver Nitrate Solution** : white, curdy precipitate of silver citrate $Ag_3.C_6H_5O_7$ from neutral solutions. The precipitate is soluble in ammonium hydroxide solution, and this solution undergoes only very slight reduction to silver on boiling (distinction from tartrate).

$$Na_3.C_6H_5O_7 + 3AgNO_3 = Ag_3.C_6H_5O_7 + 3NaNO_3.$$

3. **Calcium Chloride Solution** : no precipitate with neutral solutions in the cold (difference from tartrate), but on boiling for several minutes a crystalline precipitate of calcium tartrate $Ca_3(C_6H_5O_7)_2,4H_2O$ is produced. If sodium hydroxide solution is added to the cold solution containing excess of calcium chloride, there results an immediate precipitation of amorphous calcium citrate, insoluble in solutions of caustic alkalis, but soluble in ammonium chloride solution ; on boiling the ammonium chloride solution, crystalline calcium citrate is precipitated, which is now insoluble in ammonium chloride solution.

$$2Na_3.C_6H_5O_7 + 3CaCl_2 = 3Ca_3(C_6H_5O_7)_2 + 6NaCl.$$

4. **Cadmium Chloride Solution** : white, gelatinous precipitate of cadmium citrate $Cd_3(C_6H_5O_7)_2$, practically insoluble in boiling water, but readily soluble in warm acetic acid (tartrate gives no precipitate).

$$2Na_3.C_6H_5O_7 + 3CdCl_2 = Cd_3(C_6H_5O_7)_2 + 6NaCl.$$

5. **Denigès' Test.**—Add 1 c.c. of acid mercuric sulphate solution to 5 c.c. of the citrate solution, heat to boiling, and then add a few drops of a 2% solution of potassium permanganate. Decolourisation of the permanganate will take place rapidly and then, somewhat suddenly, a heavy white precipitate, consisting of the double salt of basic mercuric sulphate with mercuric acetone dicarboxylate

$$HgSO_4,2HgO,2[CO(CH_2.CO_2)_2Hg],$$

is formed. Salts of the halogen acids interfere and must therefore be removed before carrying out the test.

The *reagent* (an acid solution of mercuric sulphate) is prepared by adding 10 c.c. of concentrated sulphuric acid slowly to 50 c.c. of water, and dissolving 2·5 g. of mercuric oxide in the hot solution.

6. **Action of Heat.**—Citrates and citric acid char on heating ; carbon monoxide, carbon dioxide and acrid-smelling vapours are evolved.

IV, 40.**REACTIONS OF SALICYLATES, $C_6H_4(OH)CO_2^-$ OR $C_7H_5O_3^-$

Solubility.—Salicylic acid $C_6H_4(OH)CO_2H$ (*o*-hydroxybenzoic acid) forms colourless needles, which melt at 155°. The acid is sparingly soluble in cold water, but more soluble in hot water, from which it can be recrystallised. It is readily soluble in alcohol and ether. With the exception of the lead, mercury, silver and barium salts, the monobasic salts $C_6H_4(OH)CO_2M$—these are the most commonly occurring salts—are readily soluble in cold water.

Use sodium salicylate, $C_6H_4(OH)CO_2Na$ or $Na.C_7H_5O_3$.

1. **Concentrated Sulphuric Acid** : dissolves on warming ; charring occurs slowly, accompanied by the evolution of carbon monoxide and sulphur dioxide.

2. **Concentrated Sulphuric Acid and Methyl Alcohol (" Oil of Winter Green " Test).**—When 0·5 gram of a salicylate or of salicylic acid is treated with a mixture of 1·5 c.c. of concentrated sulphuric acid and 3 c.c. of methyl alcohol and the whole gently warmed, the characteristic, fragrant odour of the ester, methyl salicylate (I) (" oil of winter green "), is obtained. The odour is readily detected by pouring the mixture into dilute sodium carbonate solution contained in a porcelain dish.

$$C_6H_4(OH)CO_2H + CH_3OH \rightleftharpoons C_6H_4(OH)CO_2CH_3\ (I) + H_2O$$

(the sulphuric acid acts as a dehydrating agent).

3. **Dilute Hydrochloric Acid*** : crystalline precipitate of salicylic acid from solutions of the salts. The precipitate is moderately soluble in hot water, from which it crystallises on cooling.

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* Or any other mineral acid.

4. **Silver Nitrate Solution** : heavy, crystalline precipitate of silver salicylate $Ag.C_7H_5O_3$ from neutral solutions ; it is soluble in boiling water and crystallises from the solution on cooling.

$$C_6H_4(OH)CO_2Na + AgNO_3 = C_6H_4(OH)CO_2Ag + NaNO_3.$$

5. **Ferric Chloride Solution** : intense violet-red colouration with neutral solutions of salicylates or of free salicylic acid ; the colour disappears upon the addition of dilute mineral acids, but not of a little acetic acid. The presence of a *large* excess of many organic acids (acetic, tartaric and citric) prevents the development of the colour, but the addition of a few drops of ammonium hydroxide solution will cause it to appear.

6. **Dilute Nitric Acid.**—When a salicylate or the free acid is boiled with dilute nitric acid (1 : 5) and the mixture poured into 4 times its volume of cold water, a crystalline precipitate of 5-nitro-salicylic acid (I) is obtained. The precipitate is filtered off and recrystallised from boiling water ; the acid, after drying, has a melting point of 226°.

$$C_6H_4(OH)CO_2H + HNO_3 = C_6H_3(NO_2)(OH)CO_2H \text{ (I)} + H_2O.$$

7. **Soda Lime.**—When salicylic acid or one of its salts is heated with excess of soda lime in an ignition tube, phenol $CH_5(OH)$ is evolved, which may be recognised by its characteristic odour.

$$C_6H_4(OH)CO_2Na + NaOH = C_6H_5OH + Na_2CO_3.$$

8. **Action of Heat.**—Salicylic acid, when gradually heated above its melting point, sublimes. If it is rapidly heated, it is decomposed into carbon dioxide and phenol (II). Salicylates char on heating and phenol is evolved.

$$C_6H_4(OH)CO_2H = C_6H_5OH \text{ (II)} + CO_2.$$

IV, 41. **REACTIONS OF BENZOATES, $C_6H_5.CO_2^-$ OR $C_7H_5O_2^-$

Solubility.—Benzoic acid, $C_6H_5.CO_2H$ or $H.C_7H_5O_2$, is a white, crystalline solid ; it has a melting point of 121° and sublimes at a somewhat higher temperature. The acid is sparingly soluble in cold water, but more soluble in hot water, from which it crystallises out on cooling ; it is soluble in alcohol and in ether. All the benzoates, with the exception of the silver and basic ferric salts, are readily soluble in cold water.

Use potassium benzoate, $C_6H_5.CO_2K$ or $K.C_7H_5O_2$.

1. **Concentrated Sulphuric Acid** : no charring occurs on heating ; the acid forms a sublimate on the sides of the test-tube and irritating fumes are evolved.

2. **Dilute Sulphuric Acid*** : white, crystalline precipitate of benzoic acid from cold solutions of benzoates. The acid may be filtered off, dried between filter paper or upon a porous tile, and identified by means of its melting point (121°). If the latter is somewhat low, it may be recrystallised from hot water.

$$C_6H_5.CO_2K + HCl = C_6H_5.CO_2H + KCl.$$

3. **Concentrated Sulphuric Acid and Ethyl Alcohol.**—Heat 0·5 g. of a benzoate or of benzoic acid with a mixture of 1·5 c.c. of concentrated sulphuric acid and 3 c.c. of ethyl alcohol for a few minutes. Allow the mixture to cool, and note the pleasant and characteristic aromatic odour of the ester, ethyl benzoate (I). The odour is more apparent if the mixture is poured into dilute sodium carbonate solution contained in an evaporating basin ; oily drops of ethyl benzoate will separate out.

$$C_6H_5.CO_2H + C_2H_5OH \rightleftharpoons C_6H_5.CO_2C_2H_5 \text{ (I)} + H_2O.$$

4. **Silver Nitrate Solution** : white precipitate of silver benzoate $Ag.C_7H_5O_2$ from neutral solutions. The precipitate is soluble in hot water and crystallises from the solution on cooling ; it is also soluble in ammonium hydroxide solution.

$$C_6H_5.CO_2K + AgNO_3 = C_6H_5.CO_2Ag + KNO_3.$$

5. **Ferric Chloride Solution** : buff-coloured precipitate of basic ferric benzoate (II) from neutral solutions. The precipitate is soluble in hydrochloric acid, with the simultaneous separation of benzoic acid (see reaction *2*).

$$3C_6H_5.CO_2K + 2FeCl_3 + 3H_2O$$
$$= (C_6H_5.CO_2)_3Fe.Fe(OH)_3 \text{ (II)} + 3KCl + 3HCl.$$

6. **Soda Lime.**—Benzoic acid and benzoates are decomposed when heated in an ignition tube with excess of soda lime into benzene C_6H_6, which burns with a smoky flame, and carbon dioxide, the latter combining with the alkali present.

$$C_6H_5.CO_2H + 2NaOH = C_6H_6 + Na_2CO_3 + H_2O.$$

7. **Action of Heat.**—When benzoic acid is heated in an ignition tube, it melts, sublimes and condenses in the cool parts of the tube. An irritating vapour is simultaneously evolved, but no charring occurs. If a little of the acid or of one of its salts is heated upon platinum foil or broken porcelain, it burns with a blue, smoky flame (distinction from succinate).

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* Or any other mineral acid.

IV, 42. **REACTIONS OF SUCCINATES, $C_4H_4O_4^{--}$

Solubility.—Succinic acid, $HO_2C.CH_2.CH_2.CO_2H$ or $H_2.C_4H_4O_4$ (a dibasic acid), is a white crystalline solid with a melting point of 182° ; it boils at 235° with the formation of succinic anhydride $C_4H_4O_3$ by the loss of one molecule of water. The acid is fairly soluble in water (68·4 g. per litre at 20°), but more soluble in hot water ; it is moderately soluble in alcohol and in acetone, slightly soluble in ether and sparingly soluble in chloroform. Most normal succinates are soluble in cold water ; the silver, calcium, barium and basic ferric salts are sparingly soluble.

Use sodium succinate, $C_2H_4(CO_2Na)_2$ or $Na_2.C_4H_4O_4$.

1. **Concentrated Sulphuric Acid.**—The acid or its salts dissolve in warm, concentrated sulphuric acid without charring ; if the solution is strongly heated, slight charring takes place and sulphur dioxide is evolved.

Dilute sulphuric acid has no visible action.

2. **Silver Nitrate Solution** : white precipitate of silver succinate $Ag_2.C_4H_4O_4$ from neutral solutions, readily soluble in ammonium hydroxide solution.

$$C_2H_4(CO_2Na)_2 + 2AgNO_3 = C_2H_4(CO_2Ag)_2 + 2NaNO_3.$$

3. **Ferric Chloride Solution** : light-brown precipitate of basic ferric succinate (I) with a neutral solution ; some free succinic acid is simultaneously produced, and the solution acquires an acid reaction.

$$3C_2H_4(CO_2Na)_2 + 2FeCl_3 + 2H_2O$$
$$= 2C_2H_4(CO_2)_2Fe(OH)\ (I) + 6NaCl + C_2H_4(CO_2H)_2.$$

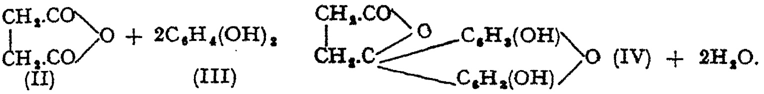
4. **Barium Chloride Solution** : white precipitate of barium succinate $Ba.C_4H_4O_4$ from neutral or slightly ammoniacal solutions (distinction from benzoate). Precipitation is slow from dilute solutions, but may be accelerated by vigorous shaking or by rubbing the inner wall of the test-tube with a glass rod.

$$C_2H_4(CO_2Na)_2 + BaCl_2 = C_2H_4(CO_2)_2Ba + 2NaCl.$$

5. **Calcium Chloride Solution** : a precipitate of calcium succinate is very slowly produced from concentrated neutral solutions.

6. **Fluorescein Test.**—About 0·5 gram of the acid or one of its salts is mixed with 1 gram of resorcinol, a few drops of concentrated sulphuric acid added, and the mixture gently heated; a deep-red solution is formed. On pouring the latter into a large volume of water, an orange-yellow solution is obtained, which exhibits an intense green fluorescence. The addition of excess of sodium hydroxide solution intensifies the fluorescence, and the colour of the solution changes to bright red.

Under the influence of concentrated sulphuric acid, succinic anhydride (II) is first formed, and this condenses with the resorcinol (III) to yield succinylfluorescein (IV).



7. **Action of Heat.**—When succinic acid or its salts are strongly heated in an ignition tube, a white sublimate of succinic anhydride $C_4H_4O_3$ is formed, and irritating vapours are evolved. If the ignition is carried out on platinum foil or upon broken porcelain, the vapour burns with a non-luminous, blue flame, leaving a residue of carbon (distinction from benzoate).

IV, 43. REACTIONS OF HYDROGEN PEROXIDE, H_2O_2

This substance is marketed in the form of " 10, 20, 40 and 100-volume " solutions. It may be obtained by adding sodium peroxide in small portions to ice water :

$$Na_2O_2 + 2H_2O = H_2O_2 + 2NaOH.$$

Owing to the heat liberated in the reaction, part of the hydrogen peroxide is decomposed :

$$2H_2O_2 = 2H_2O + O_2.$$

If this solution is to be employed for the tests to be described below, it should be acidified with ice-cold dilute sulphuric acid. Sodium peroxide sometimes contains unchanged metallic sodium, which will liberate hydrogen in contact with water and may therefore lead to a serious explosion if a light is applied to the gas evolved from the mixture.

Use a dilute solution of hydrogen peroxide.

1. **Perchromic Acid Test.**—If an acidified solution of hydrogen peroxide is mixed with a little ether (*highly inflammable*) or ethyl acetate or amyl alcohol, and a few drops of potassium dichromate solution added and the mixture gently shaken, the upper organic layer is coloured a beautiful blue. The test will detect 0·1 mg. of hydrogen peroxide.

If ether is employed, a blank test must always be carried out with the ether alone because after standing it may contain organic peroxides which give the test. *The peroxides in ether may be removed* by shaking with a solution containing 60 g. of $FeSO_4,7H_2O$, 6 c.c. of concentrated H_2SO_4 and 110 c.c. of water, then with chromic acid solution (to oxidise any acetaldehyde produced), washing with alkali, and redistilling. The use of amyl alcohol is, however, to be preferred.

2. **Potassium Iodide-Starch Test.**—If hydrogen peroxide is added to a solution containing potassium iodide and starch and acidified, a blue colouration of " starch iodide " appears.

$$2KI + H_2O_2 + H_2SO_4 = I_2 + K_2SO_4 + 2H_2O.$$

3. **Potassium Permanganate Solution** : decolourised in acid solution and oxygen is evolved.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

4. **Titanic Sulphate Solution** : orange-red colouration (see under Titanium, Section **VII, 12,** reaction *6*). This is a very delicate test.

The *titanic sulphate solution* may be prepared by heating titania with three times its volume of concentrated sulphuric acid, cooling, diluting cautiously with ice water and filtering, if necessary.

5. **Potassium Ferricyanide-Ferric Chloride Test.**—If a nearly neutral solution of pure ferric chloride is treated with a little pure potassium ferricyanide and the resultant yellow solution mixed with a nearly neutral solution of hydrogen peroxide, the mixture will assume a green colouration and then, on standing, Prussian blue will separate.

$$2[Fe(CN)_6]^{---} + H_2O_2 = 2[Fe(CN)_6]^{----} + 2H^+ + O_2.$$

Other substances, *e.g.*, stannous chloride, sodium sulphite and sodium thiosulphate, will reduce potassium ferricyanide to potassium ferrocyanide so that this reaction alone is not always a reliable test.

† The spot-test technique is as follows. In adjacent depressions of a spot plate place a drop of distilled water and a drop of the test solution. Add a drop of the reagent (equal volumes of 0·5 per cent ferric chloride solution and 0·8 per cent potassium ferricyanide solution) to each. A blue colouration or precipitate is formed.

Sensitivity : 0·1 μg. H_2O_2. Concentration limit : 1 in 600,000.

6. **Gold Chloride Solution** : reduced to finely-divided metallic gold, which appears greenish-blue by transmitted light and brown by reflected light.

$$2AuCl_3 + 3H_2O_2 = 2Au + 6HCl + 3O_2.$$

† The spot-test technique is as follows. Mix a drop of the neutral test solution with a drop of 0·01 per cent gold chloride solution in a micro-crucible and warm. After a short time, the solution is coloured red or blue with colloidal gold.

Sensitivity: 0·07 μg. H_2O_2. Concentration limit: 1 in 700,000.

†*7.* **Lead Sulphate Test.**—Hydrogen peroxide converts black lead sulphide into white lead sulphate:

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

Place a drop of the neutral or slightly acid test solution upon drop-reaction paper impregnated with lead sulphide. A white spot is formed on the brown paper.

Sensitivity: 0·04 μg. H_2O_2. Concentration limit: 1 in 1,250,000.

The **lead sulphide paper** is prepared by soaking drop-reaction paper in a 0·05 per cent solution of lead acetate, exposing it to a little hydrogen sulphide gas, and then drying in a vacuum desiccator. The paper will keep in a stoppered bottle.

IV, 44 SPECIAL TESTS FOR MIXTURES OF ACID RADICALS*

1. **Carbonate in the presence of Sulphite.**—Sulphites, on treatment with dilute sulphuric acid, liberate sulphur dioxide which, like carbon dioxide, produces a turbidity with lime water. The dichromate test for sulphites is, however, not influenced by the presence of carbonates. To detect carbonates in the presence of sulphites, treat the solid mixture with dilute sulphuric acid and pass the evolved gases through a small wash-bottle or boiling tube containing potassium dichromate solution and dilute sulphuric acid. The solution will be turned green and the sulphur dioxide will, at the same time, be completely removed; the residual gas is then tested with lime water in the usual manner.

An alternative procedure is to add a little solid potassium dichromate or a few c.c. of 10-volume hydrogen peroxide to the mixture and then to warm with dilute sulphuric acid; the evolved gas is then passed through lime water.

The above method can, of course, be applied in the presence of thiosulphates.

2. **Nitrate in the presence of Nitrite.**—The nitrite is readily identified in the presence of a nitrate by treatment with dilute mineral acid, potassium iodide and starch paste (or potassium iodide—starch paper). The nitrate cannot, however, be detected in the presence of a nitrite since the latter gives the brown ring test with ferrous sulphate solution and *dilute* sulphuric acid. The nitrite is therefore completely decomposed first by one of the following methods :—

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* Full experimental details of the various tests referred to in this section will be found under the reactions of the anions.

(i) boil with ammonium chloride solution until effervescence ceases * ;

(ii) warm with urea and dilute sulphuric acid until evolution of gas ceases * ;

(iii) add the solution to solid hydrazine sulphate ; reaction takes place in the cold, and the danger of slight oxidation of nitrite to nitrate is thereby avoided.

$$N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O\,;$$
$$N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O.$$

The nitrate can then be tested for by the brown ring test.

3. **Nitrate in the presence of Bromide and Iodide.**—The brown ring test for nitrates cannot be applied in the presence of bromides and iodides since the liberation of the free halogen with concentrated sulphuric acid will obscure the brown ring due to the nitrate. The solution is therefore boiled with sodium hydroxide solution until ammonium salts, if present, are completely decomposed ; powdered Devarda's alloy or aluminium powder is then added and the solution gently warmed. The evolution of ammonia, detected by its smell and its action upon mercurous nitrate paper (see Section **III, 36,** reaction *1*) and upon red litmus paper, indicates the presence of a nitrate.

An alternative method is to remove the halides by adding ammoniacal silver sulphate solution (this reagent contains $[Ag(NH_3)_2]_2SO_4$, and provides a high concentration of Ag^+ ions ; it is prepared by dissolving nitrate-free Ag_2SO_4 in the *minimum* volume of dilute NH_4OH solution), adding concentrated H_2SO_4 cautiously, filtering off the precipitated silver halides and excess of Ag_2SO_4, and then applying the brown ring test.

4. **Nitrate in the presence of Chlorate.**—The chlorate obscures the brown ring test. The nitrate is reduced to ammonia as described under *3* ; the chlorate is at the same time reduced to chloride, which may be tested for with silver nitrate solution and dilute nitric acid.

If a chloride is originally present, it may be removed first by the addition of silver sulphate solution.

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* *Traces* of nitrate are always formed in this reaction.

5. **Chloride in the presence of Bromide and/or Iodide.**—*Method A*. Warm the solid mixture* with a little potassium dichromate and concentrated sulphuric acid in a small distilling flask (Fig. 43), and pass the vapours, which contain chromyl chloride, into sodium hydroxide solution.‡ Test for chromate, which proves the presence of a chloride, with hydrogen peroxide and ether or with the diphenylcarbazide reagent.

The bromide and iodide yield the free halogen by this treatment; these react with the alkali. They are removed by acidifying with dilute sulphuric acid and boiling the mixture before applying the chromate test.

Method B. This procedure involves the removal of the bromide and iodide with potassium or ammonium persulphate in the presence of dilute sulphuric acid. The free halogens are thus liberated, and may be removed either by simple evaporation (addition of water may be necessary to maintain the original volume) or by evaporation at about 80° in a stream of air.

$$K_2S_2O_8 + 2KI = I_2 + 2K_2SO_4 ;$$

$$K_2S_2O_8 + 2KBr + 2H_2SO_4 = Br_2 + 4KHSO_4.$$

Add solid potassium persulphate and dilute sulphuric acid to the neutral solution of the mixed halides contained in a conical flask; heat the flask to about 80°, and aspirate a current of air through the solution with the aid of a filter pump until the solution is colourless (Fig. 44; *T* is a drawn-out capillary tube). Add more potassium persulphate or water as may be found necessary. Test the residual colourless liquid for chloride with silver nitrate solution and dilute nitric acid.**

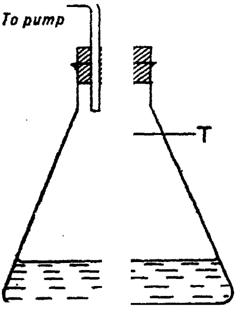

Fig. 44.

Method C. Acidify the neutral solution (see *19*; also Section **V, 4**) of the halides with dilute nitric acid, add excess

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[*] If a solution is being analysed, it should be evaporated to dryness before applying these tests. Chlorates must, of course, be absent.

[‡] Ammonia solution must not be used because of the danger of forming explosive "nitrogen iodide" when iodides are present.

[**] In a modification of this method, lead dioxide is substituted for potassium persulphate. The solution is acidified with acetic acid, lead dioxide added, and the mixture boiled until bromine and iodine are no longer evolved. Filter, and test the filtrate, which should be colourless, with silver nitrate solution and dilute nitric acid.

of silver nitrate solution, filter and wash until the washings no longer give the reactions of silver ions. Shake the precipitate with ammonium carbonate solution, filter, and add a few drops of potassium bromide solution to the filtrate; a yellowish-white precipitate of silver bromide is obtained if a *chloride* is present.

The hydrolysis of the ammonium carbonate in aqueous solution gives rise to free dilute ammonium hydroxide solution in which silver chloride, but not silver bromide or silver iodide, is appreciably soluble. The addition of bromide ions to the solution of silver chloride in ammonia results in the solubility product of silver bromide being exceeded, and precipitation occurs.

6. **Chloride in the presence of Iodide.**—Add excess of silver nitrate solution to the neutral solution and filter; reject the filtrate. Wash the precipitate with dilute ammonium hydroxide solution and filter again. Add dilute nitric acid to the washings; a white precipitate of silver chloride indicates the presence of chloride.

The separation is based upon the solubility of silver chloride in dilute ammonium hydroxide solution and the practical insolubility of silver iodide in this reagent.

7. **Bromide and Iodide in the presence of each other and of Chloride.**—The presence of a chloride does not interfere with the reactions described below. Add 1–2 drops of chlorine water (the solution obtained by carefully acidifying a solution of sodium hypochlorite may also be used) and 2–3 c.c. of chloroform or carbon tetrachloride; shake; a violet colour indicates iodide. Continue the addition of chlorine water *drop by drop* to oxidise the iodine to iodate and shake after each addition. The violet colour will disappear, and a reddish-brown colouration of the chloroform or carbon tetrachloride, due to dissolved bromine, will be obtained if a bromide is present. If iodide alone is present, the solution will be colourless after the violet colour has disappeared.

8. **Chloride, Chlorate and Perchlorate in the presence of each other.**—Each acid radical (anion) must be tested for separately. Divide the neutral solution (see *19*) into 3 parts.

(i) *Chloride.*—Add silver nitrate solution and dilute nitric acid; white precipitate of silver chloride. Silver chlorate and perchlorate are soluble in water.

(ii) *Chlorate.*—Add a few drops of dilute sulphuric acid, a little indigo solution and then sulphurous acid solution; the indigo is bleached.

An alternative method is either (*a*) to add excess of silver nitrate solution, filter, and then add dilute sulphuric acid and zinc to the filtrate; a white curdy precipitate of silver chloride will appear as the chlorate is reduced, or (*b*) add 2–3 c.c. of dilute nitric acid and a few c.c. of 5–10% formaldehyde solution, and heat to boiling; a white precipitate of silver chloride will form if a chlorate is present.

$$KClO_3 + 3H.CHO = KCl + 3H.CO_2H.$$

(iii) *Perchlorate.*—Pass excess of sulphur dioxide into the solution to reduce chlorate to chloride, boil off the excess of sulphur dioxide, and precipitate the chloride with silver sulphate solution, afterwards removing the excess of silver with a solution of sodium carbonate. Evaporate the resulting solution to dryness and heat to dull redness to convert the perchlorate into chloride. Extract the residue with water, and test for chloride with silver nitrate solution and dilute nitric acid.

9. **Iodate and Iodide in the presence of each other.**—The addition of dilute acid to a mixture of iodate and iodide results in the separation of free iodine, due to the interaction between the liberated iodic and hydriodic acids.

$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

Neither iodates nor iodides alone do this when acidified with dilute hydrochloric, sulphuric or acetic acids in the cold.

Test for iodide in the neutral solution by the addition of a few drops of chlorine water and 2–3 c.c. of chloroform or carbon tetrachloride; the latter is coloured violet. Add excess of silver sulphate solution to another portion of the neutral solution and filter off the silver iodide; remove the excess of silver sulphate with sodium carbonate solution. Pass sulphur dioxide into the filtrate to reduce iodate to iodide, boil off the excess of sulphur dioxide, and add silver nitrate solution and dilute nitric acid. A yellow precipitate of silver iodide confirms the presence of iodate in the original substance.

10. **Phosphate in the presence of Arsenate.**—Both arsenate and phosphate give a yellow precipitate on warming with ammonium molybdate solution and nitric acid, the latter on gentle warming and the former on boiling.

Acidify the neutral solution with dilute hydrochloric acid, pass in sulphur dioxide to reduce the arsenate to arsenite, boil off the excess of sulphur dioxide (test with potassium dichromate paper), and pass hydrogen sulphide into the solution to precipitate the arsenic as arsenious sulphide; continue the passage of hydrogen sulphide until no more precipitate forms. Filter, boil off the hydrogen sulphide, and test the filtrate for phosphate by the ammonium molybdate test or with magnesia mixture.

An alternative method for the elimination of arsenate is the following. Acidify the *prepared* solution with dilute hydrochloric acid and then add about one-quarter of the volume of concentrated hydrochloric acid (the total volume should be about 20 c.c.). Add 1 c.c. of 5 % ammonium iodide solution, heat to boiling, and pass hydrogen sulphide into the boiling solution until precipitation is complete (5–10 minutes). Filter off the arsenious sulphide,* and boil off the hydrogen sulphide from the filtrate. Add ammonium hydroxide solution until alkaline and excess of magnesia mixture. A white precipitate indicates the presence of a phosphate.

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2;$$
$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O;$$
$$2I_2 + 2H_2S \leftrightarrows 4HI + 2S.$$

11. **Phosphate Arsenate and Arsenite in the presence of each other.**—Add excess of magnesia mixture to the neutral solution, rub the walls of the glass vessel with a glass rod, and allow to stand for 5 minutes; filter off the precipitate of magnesium ammonium phosphate and arsenate (*A*), and preserve the filtrate (*B*) which contains the arsenite. Test for arsenite in the filtrate (*B*) either by adding silver nitrate solution to the neutral solution and obtain the yellow precipitate of silver arsenite, or by acidifying with hydrochloric acid and passing in hydrogen sulphide, when a yellow precipitate of arsenious sulphide is immediately produced.

Dissolve the precipitate (*A*) in dilute hydrochloric acid, pass sulphur dioxide into the solution for a few minutes and proceed as described under *10*. Boil off the hydrogen sulphide in the filtrate from the precipitated arsenious sulphide, and either add ammonium hydroxide solution in excess, when white crystalline magnesium ammonium phosphate will be precipitated or apply the ammonium molybdate test. The precipitate of magnesium ammonium phosphate may be washed with water, and silver nitrate solution poured upon it; yellow silver phosphate will be formed.

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* This method may also be employed for the reduction of arsenates in the group precipitation of systematic qualitative analysis.

In the absence of phosphates, arsenites may be distinguished from arsenates by the magnesia mixture test.

12. **Sulphide, Sulphite, Thiosulphate and Sulphate in the presence of each other.**—Upon the addition of dilute acid to the mixture, the hydrogen sulphide, liberated from the sulphide, and the sulphur dioxide, liberated from the sulphite and thiosulphate, react and sulphur is precipitated; this complication renders the use of a special method necessary. This is most clearly given in tabular form.

A mixture of the sodium salts or the slightly alkaline solution is employed for this separation.

<table>
<tr><td colspan="4">Shake the solution with excess of freshly precipitated $CdCO_3$, and filter.</td></tr>
<tr><td rowspan="3">Residue. CdS and of $CdCO_3$. Wash and reject washings. Digest residue with dilute acetic acid to remove excess of carbonate. A yellow residue indicates sulphide. Confirm by warming with dilute HCl and test the evolved H_2S with lead acetate paper.</td><td colspan="3">Filtrate. Add $Sr(NO_3)_2$ solution* in slight excess, shake, allow to stand overnight, and filter.</td></tr>
<tr><td colspan="2">Residue. $SrSO_3$ and $SrSO_4$. Wash, treat with dilute HCl and filter.</td><td rowspan="2">Filtrate. Contains SrS_2O_3. Acidify with dilute HCl and boil; SO_2 is evolved and S is slowly precipitated.
Thiosulphate present.</td></tr>
<tr><td>Residue. $SrSO_4$. White.
Sulphate present.
Confirm by fusion with Na_2CO_3 and apply sodium nitroprusside test.</td><td>Filtrate. Contains sulphurous acid. Add a few drops of a dilute solution of iodine; the latter is decolourised.
Sulphite present.</td></tr>
</table>

An alternative procedure for the **removal of the sulphide** is the following. Treat the solution of the sodium salts with a solution of zinc hexammine hydroxide $[Zn(NH_3)_6](OH)_2$ (prepared by adding ammonium hydroxide solution to zinc nitrate solution until the initial precipitate of zinc hydroxide has redissolved, and then adding a further excess:

$$Zn(OH)_2 + 6NH_4OH = [Zn(NH_3)_6](OH)_2 + 6H_2O).$$

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* Solubility in grams per litre: SrS_2O_3, 250 at 13°; $SrSO_3$, 0·033 at 17°.

when zinc sulphide will be precipitated and is filtered off. The precipitate may be treated with dilute hydrochloric acid and a few drops of copper sulphate solution, when a black precipitate of cupric sulphide will indicate sulphide, or it may be tested for sulphide in the usual manner.

A simple method for **separating sulphite and sulphate** consists in acidifying the neutral solution of the alkali salts with dilute hydrochloric acid and adding excess of barium chloride solution ; the sulphate is precipitated as barium sulphate, and is removed by filtration. The production of a further precipitate of barium sulphate upon the addition to the filtrate of a little concentrated nitric acid or of bromine water and warming, proves the presence of sulphite.

13. **Sulphide, Sulphite and Thiosulphate in the presence of each other.**—It is assumed that the solution is slightly alkaline and contains the sodium salts of the anions.

(i) Test a portion of the solution for sulphide with sodium nitroprusside solution. The formation of a purple colouration indicates the presence of a **sulphide.**

(ii) If sulphide is present, remove it by shaking with freshly precipitated cadmium carbonate and filter. Test a portion of the filtrate with sodium nitroprusside solution to see that all the sulphide has been removed. When no sulphide is present, treat the remainder of the filtrate with a drop of phenolphthalein solution and pass in carbon dioxide until the solution is decolourised by it. Test 2–3 c.c. of the colourless solution with fuchsin-malachite green reagent. If the solution of the dyestuffs is decolourised, the presence of **sulphite** is indicated.

The *fuchsin-malachite green reagent* is prepared by mixing 3 volumes of a 0·025 per cent aqueous solution of fuchsin with 1 volume of 0·025 per cent aqueous malachite green solution.*

(iii) Treat the remainder of the colourless solution with dilute hydrochloric acid and boil for a few minutes. If sulphur separates, a **thiosulphate** is indicated. Alternatively, the nickel ethylenediamine nitrate test (Section **IV, 5,** reaction *9*) may be applied.

14. **Borate in the presence of Copper and Barium Salts.**—When carrying out the ethyl borate test for borates (Section

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* Sulphides decolourise the reagent, hence they must be removed before the test is applied.

IV, 23, reaction 2), it must be remembered that copper and barium salts may also impart a green colour to the alcohol flame. The test is best carried out in the following way when salts of either or both of these metals are present. The mixture of the borate, concentrated sulphuric acid and ethyl alcohol is placed in a small round-bottomed flask, fitted with a glass jet and surmounted by a wide glass tube, which acts as a "chimney" (Fig. 45). The mixture is gently warmed, and the vapours ignited at the top of the wide glass tube.

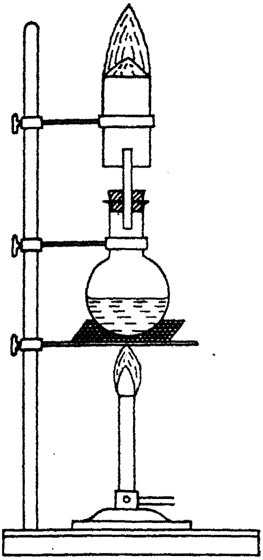

Fig. 45.

A green flame confirms the presence of a borate.

15. **Fluoride, Silicofluoride and Sulphate in the presence of each other.**—The following differences in solubilities of the lead salts are utilised in this separation : lead silicofluoride is soluble in water ; lead fluoride is insoluble in water but soluble in dilute acetic acid ; lead sulphate is insoluble in water and in boiling dilute acetic acid.

Add excess of lead acetate solution to the solution of the alkali metal salts, and filter cold.

Residue. Wash well with cold water. Divide into two parts. (i) *Smaller portion.* Add excess of dilute acetic acid and boil (this will dissolve any lead fluoride). White residue indicates **sulphate.** (ii) *Larger portion.* Treat cautiously with concentrated sulphuric acid and test with a moist glass rod. Milkiness of the water and etching of the tube indicates **fluoride.**	**Filtrate.** Add $Ba(NO_3)_2$ solution and warm gently. White crystalline precipitate indicates **silicofluoride**

16. **Oxalate in the presence of Fluoride.**—Both calcium fluoride and calcium oxalate are precipitated by ammonium oxalate solution in the presence of dilute acetic acid. The fluoride may be identified in the usual manner with concentrated sulphuric acid. The oxalate is most simply detected by dissolving a portion of the precipitate in hot dilute sulphuric acid and then adding a few drops of a very dilute solution of potassium permanganate. The latter will be decolourised if an oxalate is present.

17. **Chloride and Cyanide in the presence of each other.**—Both silver chloride and silver cyanide are insoluble in water, but soluble in dilute ammonium hydroxide solution. Three methods are available for the detection of cyanide in the presence of chloride.

(i) The concentrated solution, or preferably the solid mixture of sodium salts, is treated with about 5 times its weight of 100 volume hydrogen peroxide and the mixture gently warmed; ammonia is evolved, which is recognised by its action upon mercurous nitrate paper. The solution is then boiled to decompose all the hydrogen peroxide, and then tested for chloride with silver nitrate solution and dilute nitric acid.

$$NaCN + H_2O_2 = NaCNO + H_2O;$$

$$NaCNO + 2H_2O = NaHCO_3 + NH_3.$$

(ii) The cyanide is precipitated as the pale green nickel cyanide by the addition of excess of a solution of nickel sulphate to the neutral solution; the whole is filtered and the excess of nickel sulphate removed by boiling with sodium hydroxide solution and filtering off the precipitate of nickel hydroxide. The filtrate is acidified with dilute nitric acid and excess of silver nitrate solution added. A white, curdy precipitate of silver chloride confirms the presence of chloride.

(iii) The solution of the mixed sodium salts is treated with excess of solid sodium bicarbonate (see Fig. 43), the mixture warmed, and the evolved hydrogen cyanide passed into silver nitrate solution acidified with dilute nitric acid; a white precipitate of silver cyanide is obtained. This method can be employed in the presence of ferrocyanides, ferricyanides and thiocyanates.

For the detection of cyanide, chloride, bromide and iodide in the presence of one another the cyanide is first completely removed, and the separation of chloride, bromide and iodide carried out as detailed under *7*.

The cyanide can also be detected by the usual Prussian blue test with solutions of ferrous sulphate, ferrous chloride and hydrochloric acid.

18. Ferrocyanide, Ferricyanide and Thiocyanate in the presence of each other.—

<table>
<tr><td colspan="3">The neutral solution of the sodium salts is acidified with acetic acid, excess of a solution of thorium nitrate and finely divided asbestos or filter paper pulp added, and the whole well shaken ; filter.</td></tr>
<tr><td rowspan="2">Residue. $Th[Fe(CN)_6]$ and asbestos or filter paper pulp (the latter are added to facilitate filtration of the gelatinous precipitate). Wash with a little cold water. Treat the ppt. on the filter paper with dilute NaOH solution ; acidify the alkaline extract with dilute HCl and add a few drops of $FeCl_3$ solution.
A precipitate of Prussian blue indicates ferrocyanide.</td><td colspan="2">Filtrate. Add $CdSO_4$ solution and finely divided asbestos, shake, filter.</td></tr>
<tr><td>Residue. Orange: $Cd_3[Fe(CN)_6]_2$ and asbestos. Extract with NaOH solution, acidify extract with dilute HCl, add freshly prepared $FeSO_4$ solution. Ppt of Turnbull's blue indicates ferricyanide.</td><td>Filtrate. Add $FeCl_3$ solution and ether. Red colouration of ether proves presence of thiocyanate.</td></tr>
</table>

19. **Separation of Organic Acids (Oxalate, Tartrate, Citrate, Benzoate, Succinate, Acetate, Formate and Salicylate in the presence of each other).**—Prepare a *neutral solution* of the salts as follows. Intimately mix the mixture of acids and/or their salts with 6–7 times the bulk of anhydrous sodium carbonate, add just sufficient water to dissolve the carbonate, heat under reflux for 15 minutes, and filter. Wash and neglect residue. Acidify filtrate and washings with dilute nitric acid, boil to expel carbon dioxide, and add ammonium hydroxide solution until just alkaline. Boil off excess of ammonia ; a neutral solution,* free from heavy metals, is thus obtained.

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* See Section **V, 17,** test **5,** for a slightly different procedure.

<table>
<tr><td colspan="6">Add $CaCl_2$ solution to the cold neutral solution, rub sides of vessel with a glass rod, allow to stand for 10 minutes with occasional shaking ; filter.</td></tr>
<tr><td colspan="2">Residue. May be Ca oxalate (formed immediately) or Ca tartrate (formed on standing)[‡]. Wash. Boil with dilute acetic acid and filter.</td><td colspan="4">Filtrate. Add more $CaCl_2$ solution, boil under reflux for at least 5 minutes. A ppt. may form gradually ; filter.</td></tr>
<tr><td rowspan="2">Residue. CaC_2O_4. Dissolve in a little dilute HCl, add NH_4OH in slight excess. White ppt., insoluble in dilute acetic acid. Oxalate present. Confirm by resorcinol test, or by decolourisation of dilute solution of acidified $KMnO_4$ at 60–70°.</td><td rowspan="2">Filtrate. May contain Ca tartrate. Test neutral solution with Fenton's reagent, violet colouration (see Note), or by silver mirror test for tartrate. Confirm by copper hydroxide test.</td><td rowspan="2">Residue. Ca citrate. White. Citrate present. Divide into 2 parts. (i) Confirm by Denigès' test. (ii) Dissolve in dilute HCl, convert into neutral solution with NH_4OH, etc., and add $CdCl_2$ solution. White gelatinous precipitate.</td><td colspan="3">Filtrate. If citrate present, evaporate to dryness on water bath, add a little cold water, and filter from any residue of Ca citrate.
If citrate absent, proceed with solution.
Add $FeCl_3$ solution ; filter (if necessary).</td></tr>
<tr><td>Residue. Ferric benzoate and/or ferric succinate. Separate by procedure <i>A</i>.</td><td>Residue. Basic ferric formate and basic ferric acetate. Separate by procedure <i>B</i>.</td><td>Filtrate. Coloured.
(<i>a</i>) Violet—salicylate. Confirm by "oil of winter green" test.
(<i>b</i>) Deep blue or greenish black—gallate or tannate.[*]</td></tr>
</table>

Procedure A.

Separation of benzoate and succinate.—The precipitated ferric salts are boiled with a little dilute ammonium hydroxide solution, the precipitated ferric hydroxide filtered off and discarded, and the excess of ammonia boiled off from the filtrate. The filtrate is divided into two parts.

One portion is treated with barium chloride solution and any precipitate formed is filtered off. The residue consists of barium *succinate*. The succinate is confirmed by the fluorescein test. The second portion of the solution is acidified with dilute hydrochloric acid, when ***benzoic acid*** will separate out on cooling. It can be identified by its melting point.

[‡] It must be remembered that phosphates, fluorides, sulphates, etc., are precipitated by calcium chloride solution.

[*] Gallates and tannates are of rare occurrence in general qualitative analysis.

Procedure B.

Formates and Acetates in the presence of each other

Formate. (i) *In the absence of tartrates, citrates and reducing agents.* Add silver nitrate solution to the neutral solution; a white precipitate, which is converted into a black deposit of silver on boiling, indicates *formate.* A little of the solid substance may be treated with concentrated sulphuric acid, when carbon monoxide (burns with blue flame) will be evolved in the cold.

(ii) *In the presence of tartrates, citrates and reducing agents.* Acidify the mixture with dilute sulphuric acid and distil. A solution of the free acids will pass over. Neutralise distillate with ammonium hydroxide solution, boil off excess of ammonia (if necessary) and test as in (i).

Acetate. If other organic acids are present, obtain the solution of mixed acids as in (ii); otherwise, use the neutral solution. Boil under reflux with an equal volume of potassium dichromate solution and dilute sulphuric acid; this will decompose the formic acid. Distil off the acetic acid, neutralise, and test with ferric chloride solution.

If the solid is available, the cacodyl test may be employed.

Note.—With Fenton's reagent and a neutral solution of a citrate, a yellow or brown colour is obtained, but there is no precipitation of iron; with an oxalate, the iron is precipitated as the hydroxide.

CHAPTER V

SYSTEMATIC QUALITATIVE ANALYSIS OF INORGANIC SUBSTANCES

In the scheme of analysis to be described in the following pages, it is assumed that the student is already familiar with the tests and operations described in the preceding chapters. It will be shown how these isolated facts are incorporated in the systematic methods of qualitative analysis, applicable not only to simple solid substances, but also to mixtures of solid substances, to liquids, to alloys, and to " insoluble " substances, *i.e.*, substances which are insoluble in aqua regia and acid solvents.

It must be emphasised that the object of qualitative analysis is not simply to detect the constituents of a given mixture ; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose about 1 gram of the substance is usually employed for the analysis ; the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

Every analysis is divided into three parts :

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions).

(2) *The examination for metal ions* (*cations*) *in solution.*

(3) *The examination for acid radicals* (*or anions*) *in solution.*

The substance to be analysed may be: (A) *solid and non-metallic*, (B) *a liquid* (*solution*), (C) *a metal or an alloy*, and (D) *an " insoluble " substance.* All of these will be discussed separately.

V, 1. A. ANALYSIS OF SOLID AND NON-METALLIC SUBSTANCES

The appearance of the substance should be carefully noted ; a lens or microscope should be used, if necessary. Observe whether it is crystalline or amorphous, whether it is magnetic, and whether it possesses any characteristic odour or colour.

Some of the commonly occurring coloured compounds are listed below :—

Red : Pb_3O_4, As_2S_2, HgO, HgI_2, HgS, Sb_2S_3, CrO_3, Cu_2O, $K_3[Fe(CN)_6]$; dichromates are orange-red ; permanganates and chrome alum are reddish-purple.

Pink : hydrated salts of manganese and of cobalt.

Yellow : CdS, As_2S_3, SnS_2, PbI_2, HgO (precipitated), $K_4[Fe(CN)_6],3H_2O$; normal chromates ferric chloride and nitrate.

Green : Cr_2O_3, Hg_2I_2, $Cr(OH)_3$; ferrous salts, *e.g.*, $FeSO_4,7H_2O$, $FeSO_4,(NH_4)_2SO_4,6H_2O$, $FeCl_2,4H_2O$; nickel salts ; $CrCl_3,6H_2O$, $CuCl_2,2H_2O$, $CuCO_3$, K_2MnO_4.

Blue : anhydrous cobalt salts ; hydrated cupric salts ; Prussian blue.

Brown : PbO_2, CdO,Fe_3O_4, Ag_3AsO_4, SnS, Fe_2O_3 and $Fe(OH)_3$ (reddish-brown).

Black : PbS, CuS, CuO, HgS, FeS, MnO_2, Co_3O_4, CoS, NiS, Ni_2O_3, Ag_2S, C.

The colour of the solution obtained when the substance is dissolved in water or in dilute acids should be noted, as this may often give valuable information. The following colours are shown by the ions present in the dilute solution :—

Blue : cupric copper ; *green :* nickel, ferrous iron, chromic chromium, manganates ; *yellow :* chromates, ferrocyanides, ferric iron ; *orange-red :* dichromates ; *purple :* permanganates ; *pink :* cobalt, manganese.

The substance should be reduced to a fine powder in a suitable mortar before proceeding with the following tests. These tests usually give a great deal of useful information ; they are quickly performed (10–15 minutes) and should never be omitted.

V, 2. PRELIMINARY DRY TESTS

The following tests are made :—

(i) *action of heat* ; (ii) *flame colourations* ; (iii) *charcoal block reductions* ; (iv) *borax and phosphate bead reactions* ; (v) *ammonium radical test** ; (vi) *nitrate (or nitrite) test**.

Test (i). Heating in a closed tube.—Place a small quantity of the substance in a dry ignition tube so that none of it remains adhering to the sides, and heat cautiously ; the tube should be held in an almost horizontal position. The temperature is gradually raised, and any changes which take place carefully noted.

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* These are really wet tests, but are included here for the sake of convenience.

Observation	*Inference*
(a) The substance changes colour.	
1. Blackening from separation of carbon, often accompanied by burning.	Organic substances, *e.g.*, tartrates and citrates.
2. Blackening, not accompanied by burning or odour.	Cu, Mn and Ni salts at a very high temperature.
3. Yellow when hot, white when cold.	ZnO and many Zn salts.
4. Yellowish-brown when hot, yellow when cold.	SnO_2 or Bi_2O_3.
5. Yellow when hot, yellow when cold.	PbO and some Pb salts.
6. Brown when hot, brown when cold.	CdO and many Cd salts.
7. Red to black when hot, brown when cold.	Fe_2O_3.
(b) A sublimate is formed.	
1. White sublimate*.	$HgCl_2$, $HgBr_2$, Hg_2Cl_2, ammonium halides, As_2O_3, Sb_2O_3, certain volatile organic compounds (oxalic acid, benzoic acid).
2. Grey sublimate, easily rubbed to globules.	Hg.
3. Steel-grey sublimate ; garlic odour.	As.
4. Yellow sublimate.	S (melts on heating), As_2S_3, HgI_2 (red when rubbed with a glass rod).
5. Blue-black sublimate ; violet vapour.	I.
6. Black ; red on trituration.	HgS.

* If a white sublimate forms, heat with 4 times the bulk of anhydrous sodium carbonate and a little potassium cyanide in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates *Hg*; a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates *As* ; ammonia evolved (test with mercurous nitrate paper) indicates *ammonium salts*.

(c) A gas or vapour is evolved.	
1. Water is evolved ; test with litmus paper.	Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts, oxy-acids, hydroxides.
The water is alkaline.	Ammonium salts.
The water is acid.	Readily decomposed salts of strong acids, also acids.
2. Oxygen is evolved (rekindles glowing splint).	Nitrates, chlorates, perchlorates, bromates, iodates, peroxides and permanganates.
3. Nitrous oxide (rekindles glowing splint) and steam are evolved.	Ammonium nitrate or nitrate mixed with an ammonium salt.

Observation	*Inference*
4. Dark-brown or reddish fumes (oxides of nitrogen); acidic in reaction.	Nitrates or nitrites of heavy metals.
5. Carbon dioxide is evolved (lime water rendered turbid).	Carbonates, bicarbonates, oxalates and organic compounds.
6. Carbon monoxide is evolved (burns with a blue flame forming carbon dioxide); *poisonous gas.*	Oxalates.
7. Cyanogen is evolved (burns with violet flame and characteristic odour); *very poisonous gas.*	Cyanides of heavy metals, *e.g.*, of Hg and Ag; $K_3[Fe(CN)_6]$.
8. Acetone is evolved (burns with luminous flame).	Acetates.
9. Ammonia is evolved (odour; turns mercurous nitrate paper black).	Ammonium salts; certain complex ammines.
10. Phosphine is evolved (odour of rotten fish; inflammable); *very poisonous.*	Phosphites and hypophosphites.
11. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green).	Normal and acid sulphites; thiosulphates; certain sulphates.
12. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black).	Acid sulphides; hydrated sulphides.
13. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); *very poisonous.*	Unstable chlorides, *e.g.*, of Cu, Au and Pt; chlorides in presence of oxidising agents.
14. Bromine is evolved (reddish-brown vapour; choking odour).	Sources similar to chlorine.
15. Iodine is evolved (violet vapours condensing to black crystals).	Free iodine and certain iodides.

Test (ii). Flame colourations.—Place a small quantity of the substance on a watch glass, moisten with a little concentrated hydrochloric acid, and introduce a little of the sub-

Observation	*Inference*
Persistent golden-yellow flame.	Sodium.
Violet (lilac) flame.	Potassium.
Carmine-red flame.	Lithium.
Brick-red (yellowish-red) flame.	Calcium.
Crimson flame.	Strontium.
Yellowish-green flame.	Barium [molybdenum].
Green flame.	Borates, copper [thallium].
Livid blue flame (wire slowly corroded).	Lead, arsenic, antimony, bismuth, copper.

stance on a clean platinum wire into the base of the non-luminous Bunsen flame. An alternative method is to dip the platinum wire into concentrated hydrochloric acid contained in a watch glass and then into the substance; sufficient will adhere to the platinum wire for the test to be carried out.

The sodium flame masks that of other elements, *e.g.*, that of potassium. Mixtures can be readily detected with the spectroscope. A less delicate method is to view the flame through two thicknesses of cobalt blue glass, whereby the yellow colour due to sodium is masked or absorbed, and the other colours are modified as follows.

Flame Colouration	*Flame colouration through cobalt glass*	*Inference*
Golden-yellow.	Nil.	Sodium.
Violet.	Crimson.	Potassium.
Brick-red.	Light green.	Calcium.
Crimson.	Purple.	Strontium.
Yellowish-green.	Bluish-green.	Barium.

Test (iii). Charcoal block reductions.—

(*a*) Heat a little of the substance in a small cavity scooped in a charcoal block in a blowpipe flame.

Observation	*Inference*
1. The substance decrepitates.	Crystalline salts, as NaCl, KCl.
2. The substance deflagrates.	Nitrates, nitrites, chlorates, perchlorates, iodates, permanganates.
3. The substance fuses and is absorbed by the charcoal, or forms a liquid bead.	Salts of the alkalis and some salts of the alkaline earths.
4. The substance is infusible and incandescent, or forms an incrustation upon the charcoal.	Apply test (*b*) below.

(*b*) The substance is mixed with twice its bulk of anhydrous sodium carbonate, placed in a cavity of a piece of charcoal, and heated in the reducing flame of the blowpipe.

The sodium carbonate converts a metallic salt into a carbonate or oxide on heating, and thus reduction occurs more rapidly than with the charcoal alone, as in (*a*). Further, the sodium carbonate acts as a flux and, in the fused state, protects any metallic globules, which may have formed beneath it, from oxidation,

Observation	*Inference*
1. White, infusible, and incandescent when hot.	BaO, SrO, CaO, MgO (residue alkaline to litmus paper). Al_2O_3, ZnO, SiO_2 (residue not alkaline to litmus paper).
2. Incrustation without metal :	
White, yellow when hot.	ZnO.
White, garlic odour.	As_2O_3.
Brown.	CdO.
3. Incrustation with metal :	
White incrustation ; brittle metal.	Sb.
Yellow incrustation ; brittle metal.	Bi.
Yellow incrustation ; malleable metal, marks paper.	Pb.
4. Metal without incrustation :	
Grey metallic particles, attracted by magnet.	Fe, Ni, Co.
Malleable beads.	Ag and Sn (white), Cu (red flakes) [Au].

Sulphur compounds are reduced to sulphide by this treatment ; the residue may be moistened with water and placed in contact with a silver coin when a brown to black stain of silver sulphide is obtained (Hepar reaction), or it may be extracted with a little water and filtered into a freshly prepared sodium nitroprusside solution, when an unstable purple colouration will indicate the presence of sulphur (see Section **IV**, **6**, reaction *5*).

(*c*) The substance or the infusible residue of **test** (*b*) is moistened with one to two drops of cobalt nitrate solution and strongly ignited.

Observation	*Inference*
1. Blue residue.	Al_2O_3, phosphates, arsenates, silicates, borates.
2. Green residue.	ZnO.
3. Pink residue.	MgO.

Test (iv). Borax bead reactions.—A borax bead is made in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. A *small* quantity of the substance is brought into contact with the hot bead and heated in the outer or oxidising flame. The colour is observed when the bead is hot and also when it is cold. The bead is then heated in the inner or reducing flame and the colours observed in the hot and cold states.

Coloured beads are obtained with compounds of copper, iron, chromium, manganese, cobalt and nickel (see, however, Chapter VII, Section **VII, 19**, for extended table).

Oxidising Flame	*Reducing Flame*	*Metal*
1. Green when hot; blue when cold.	Colourless or opaque when cold.	Copper.
2. Yellowish-brown or red when hot; yellow when cold.	Green, hot and cold.	Iron.
3. Green, hot and cold.	Green, hot and cold.	Chromium.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Manganese.
5. Blue, hot and cold.	Blue, hot and cold.	Cobalt.
6. Reddish-brown when cold.	Grey or black and opaque when cold.	Nickel.

The presence of manganese and of chromium is confirmed by fusing the substance with sodium carbonate and potassium nitrate on platinum foil or broken porcelain. A green mass on cooling indicates *manganese*; a yellow mass, *chromium*. The sodium carbonate bead test (Section **II, 1,** *7*) may also be employed.

A useful reaction which may be carried out at this stage is the **microcosmic bead test** (Section **II, 1,** *6*). This test is carried out in a loop of platinum wire exactly as for the borax bead test. The presence of a white skeleton (of silica) in the coloured glass indicates *silicate*. Stannic oxide SnO_2 dissolves slowly in the bead and may be mistaken for silica.

Test (v). Test for the ammonium radical.—A little of the substance is boiled with sodium hydroxide solution. Ammonia, detected by its odour and its action upon litmus paper and upon filter paper soaked in mercurous nitrate solution, is evolved from ammonium salts.

The following experimental details in testing for ammonia are of value for other gases (with suitable modification of reagents). In order to avoid holding the test paper (litmus, etc.) in the vapour, the apparatus shown in Fig. 46 may be employed; the test paper is supported on the upper end of the wide glass tube. If ammonia is present, the litmus paper should show a gradual development of colour from the bottom upwards and should eventually become *uniformly* blue;

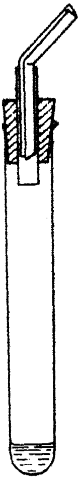

Fig. 46.

scattered blue spots indicate that droplets of the alkaline solution have come into contact with the paper. The spray may be trapped, if desired, by a loosely-fitting plug of cotton wool inserted in the upper part of the test-tube.

If the evolved gas is soluble in water and a solution is required for further testing, the apparatus shown in Fig. 43 (with the delivery tube of fairly wide tubing and about twice the length of the test-tube or distilling flask in order to avoid the danger of " sucking back ") may be employed. In the present case the ammonia may be absorbed in 3–4 c.c. of distilled water. Upon adding Nessler's reagent (Section **III, 36,** 2—the second method of preparation is recommended), an orange or brown *precipitate* ($NH_2Hg_2I_3$) confirms ammonia. This test is an extremely sensitive one and in order to establish the presence of ammonia evolved in the reaction a precipitate and not a colouration must be obtained.

V, 3. PRELIMINARY TESTS FOR ACID RADICALS (ANIONS)

The action of dilute sulphuric acid (or of dilute hydrochloric acid) and of concentrated sulphuric acid upon the substance, combined with inferences drawn from the preliminary dry tests, supply much information which may be useful in the subsequent tests, notably for cations. Thus the presence of silicate, borate, fluoride, citrate, tartrate and possibly oxalate will have been indicated—phosphates are detected in the group separation after Group II ; the course of systematic analysis for the metal ions can then be appropriately modified (see Table XXIV, and discussion in Chapter VI). The indications of the preliminary tests must, of course, be confirmed. The systematic examination for acid radicals (anions) is carried out after that of the cations.

Before describing these preliminary tests, a summary of the solubilities of the salts of the more common acids in water may be found useful in the subsequent deductions.

Nitrates, chlorates, acetates, manganates and *permanganates* are all soluble ; exceptions are a few basic nitrates (*e.g.*, Bi) and basic acetates (*e.g.*, Fe) ; silver and mercurous acetates are sparingly soluble.

Nitrites are all soluble; silver nitrite is sparingly soluble.

Chlorides are generally soluble; exceptions are AgCl, Hg_2Cl_2, Cu_2Cl_2, SbOCl, BiOCl, which are insoluble; $PbCl_2$ is sparingly soluble.

Bromides have similar solubilities to the chlorides.

Iodides are generally soluble; exceptions are AgI, Hg_2I_2, HgI_2, Cu_2I_2, BiOI, SbOI, which are insoluble; PbI_2, BiI_3 and SnI_2 are slightly soluble.

Carbonates are generally insoluble; those of Na, K and NH_4 are soluble. The *bicarbonates* of the alkali metals and of Ca, Sr, Ba, Mg, Fe and Mn are also soluble.

Sulphides are generally insoluble; those of Ba, Sr and Ca are slightly soluble; those of Na, K and NH_4 are readily soluble.

Sulphites are generally insoluble; exceptions are those of the alkali metals, and the bisulphites of the alkaline earth group.

Sulphates are generally soluble; those of Pb, Hg (ous), Sr and Ba are insoluble; those of Ag, Hg (ic), Ca and a few basic sulphates are slightly soluble.

Phosphates, arsenates and arsenites are generally insoluble; those of Na, K and NH_4 are soluble.

Fluorides are generally insoluble; those of Na, K, NH_4, Ag and Hg (ous) are soluble.

Borates, with the exception of those of the alkali metals, are insoluble.

Silicates possess solubilities similar to those of the borates.

Chromates are generally insoluble or sparingly soluble; exceptions are those of the alkali metals and Ca, Sr, Mg, Mn, Zn, Fe and Cu.

Thiocyanates of Hg (ic), Cu (ic), Fe, Ca, Sr, Ba, Mg, Na, K and NH_4 are soluble.

Thiosulphates are generally soluble; the Ag and Ba salts are sparingly soluble.

Oxalates, formates, tartrates and citrates are generally insoluble; those of Na, K and NH_4 are soluble.

Test (vi). Action of dilute sulphuric acid.—Treat 0·5–1 gram of the substance in a test-tube with dilute sulphuric acid, and note whether any reaction takes place in the cold (indicated by *C*). Warm gently and observe the effect produced.

Observation	*Inference*
1. Colourless gas is evolved with effervescence; gas is odourless and produces turbidity when passed into lime water. (*C*)	CO_2 from *carbonate.*
2. Nitrous fumes evolved; recognised by reddish-brown colour, and turning starch-potassium iodide paper bluish-black. (*C*)	NO_2 from *nitrite.*
3. Yellowish-green gas evolved; suffocating odour, reddens and then bleaches litmus paper; *very poisonous.** (*C*)	Cl_2 from *hypochlorite.*
4. Odour of acetylene; burns with luminous, smoky flame. (*C*)	C_2H_2 from *carbide.*
5. Colourless gas is evolved with suffocating odour; turns filter paper moistened with acidified potassium dichromate solution green.	SO_2 from *sulphite.*
6. Colourless gas is evolved; gives above tests for SO_2; sulphur is deposited in the solution.	SO_2 and S from *thiosulphate.*
7. Colourless gas is evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution.	H_2S from *sulphide.*
8. Colourless gas is evolved; gives above tests for H_2S; sulphur is deposited.	H_2S and S from *polysulphide.*
9. Odour of vinegar.	$H.C_2H_3O_2$ from *acetate.*
10. Colourless gas is evolved; odour of bitter almonds‡; *highly poisonous.*	HCN from *cyanide.*
11. Colourless gas is evolved; rekindles glowing splint.	O_2 from *peroxides* of alkali and alkaline earth metals.
12. Colourless gas is evolved; pungent odour, reminiscent of SO_2; produces turbidity when passed into lime water.	CO_2 and a little HCNO from *cyanate.*

Test (vii). Action of concentrated sulphuric acid.—A small quantity of the substance is treated with 2–3 c.c. of concentrated sulphuric acid, and the mixture gently warmed, the mouth of the test-tube being inclined away from the observer. (If chlorates or permanganates are suspected from the preliminary charcoal reductions tests to be present, very small quantities must be used (about 0·1 gram) as a dangerous explosion may occur on warming.)

If the substance reacted with dilute sulphuric acid, the addition of the concentrated acid may result in vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of the acid. In such a case, it is best to add dilute sulphuric acid drop-wise to another portion of the substance until action ceases, and then to add 3–4 c.c. of concentrated sulphuric acid.

The following results may be obtained.

* Also turns starch-potassium iodide paper blue.

‡ For characteristic test, see Section **IV, 8,** reaction *1*.

Observation	*Inference*
1. Colourless gas evolved with pungent odour and which fumes in the air ; white fumes of NH_4Cl in contact with glass rod wet with NH_4OH solution ; Cl_2 evolved on addition of MnO_2 (bleaches litmus paper).	HCl from *chloride.*
2. Gas evolved with pungent odour, reddish colour, and fumes in moist air ; on addition of MnO_2, increased amount of red fumes with odour of bromine (fumes colour moist starch paper orange-red).	HBr and Br_2 from *bromide.*
3. Violet vapours evolved, accompanied by pungent acid fumes, and often SO_2 and even H_2S.	HI and I_2 from *iodide.*
4. Reddish-brown fumes evolved (similar in colour to bromine) ; on passing into water, obtain chromic and hydrochloric acids, both readily identified (yellow ppt. of $PbCrO_4$ with excess of NH_4OH solution, lead acetate solution and acetic acid).	CrO_2Cl_2 from *chloride in presence of chromate.*
5. Pungent acid fumes evolved, often coloured brown by NO_2 ; colour deepens upon addition of copper turnings (if nitrites absent).	HNO_3 and NO_2 from *nitrate.*
6. Yellow gas evolved in the cold with characteristic odour ; explosion or crackling noise on warming (*danger!*).	ClO_2 from *chlorate.*
7. Yellowish-green gas evolved ; irritating odour ; bleaches litmus paper ; *very poisonous.*	Cl_2 from *chloride in presence of oxidising agents.*
8. " Oily " appearance of tube in cold ; on warming, pungent gas evolved which corrodes the glass ; if moistened glass rod introduced into the vapour, gelatinous ppt. of silicic acid is deposited upon it.	HF from *fluoride.*
9. Purple fumes evolved with explosion (*great danger!*)	Mn_2O_7 from *permanganate.*
10. Colourless gas evolved ; burns with blue flame ; no charring.	CO from *formate, cyanide, ferricyanide or ferrocyanide.*‡

[*Continued overleaf*

‡ If **ferro- and/or ferri-cyanides are present,** they must be destroyed before proceeding with the analysis for cations because they would yield precipitates when the solution is acidified and boiled, and would also introduce other disturbing effects. This may be effected by heating about 1 g. of the mixture with 3–4 c.c. of concentrated sulphuric acid in a porcelain crucible placed in an inclined position over the flame and directing the flame against the upper part of the crucible. The heating is continued until fumes of sulphur trioxide cease to be evolved. The residue is then treated with a little concentrated sulphuric acid, warmed gently and water added portion-wise. The whole is then boiled for about 5 minutes, and filtered when cold. The filtrate may be analysed for all metals except lead, strontium and barium which, if present, will be found in the residue.

Alternatively, the complex cyanides may be eliminated from the mixture by fusing with an equal weight of sodium or potassium carbonate in a porcelain crucible. Soluble cyanates and cyanides are formed, which may be extracted with water ; the residual metallic iron may be dissolved in dilute hydrochloric acid.

$$K_4[Fe(CN)_6] + K_2CO_3 = KCN + 5KCNO + CO + Fe.$$

Observation	*Inference*
11. Colourless gas evolved ; renders lime water turbid and also burns with a blue flame ; no blackening.	CO and CO_2 from *oxalate.*
12. Colourless gas evolved ; burns with a blue flame and/or renders lime water turbid ; as heating is continued, SO_2 is evolved and residue in tube (*a*) chars rapidly (odour of burnt sugar), (*b*) chars slowly, accompanied by irritant vapours.	CO, CO_2 and SO_2 from (*a*) *tartrate,* (*b*) *citrate.*
13. Irritating fumes evolved.	*Benzoate.*
14. Pungent odour of vinegar.	$H.C_2H_3O_2$ from *acetate.*
15. Dark-crimson colouration of acid.	*Gallate.*
16. Brownish-purple colouration of acid.	*Tannate.*
17. Colourless gas evolved ; rekindles glowing splint (*danger!*)	O_2 from *peroxides, iodate, chromate,* or *permanganate.*
18. Colourless gas evolved, burns with blue flame, deep blue solution produced.	CO and anhydrous $CoSO_4$ from *cobalticyanide**.
19. Colourless gas evolved, largely SO_2, and S separates (no visible action with dilute H_2SO_4).	*Thiocyanate.*

Test (viii). Test for nitrate (or nitrite).—If ammonium has been found, boiling is continued until ammonia can no longer be detected by its action upon mercurous nitrate paper or upon red litmus paper. A little aluminium powder or zinc dust or finely-powdered Devarda's alloy is then added to the cooled solution and the mixture gently warmed. Remove the flame as soon as evolution of hydrogen commences (with aluminium powder the reaction may become vigorous ; cooling with tap water may be necessary to moderate the vigour of the reaction).

If ammonia is evolved, as detected by its odour, its action upon litmus paper and upon filter paper soaked in mercurous nitrate solution,† then the presence of a nitrate or nitrite is indicated (compare Section **IV, 18,** reaction *4*). The presence of a nitrite will generally also be detected in the reaction with dilute sulphuric acid (see test (**vi**)) ; if nitrite be absent, then the presence of nitrate alone is indicated.

* Rarely encountered in routine qualitative analysis ; a characteristic test is the white precipitate, insoluble in nitrate acid, produced with ferrous sulphate solution (see under Cobalt, Section **III, 24**, reaction *4*).

† It must be emphasised that the mercurous nitrate paper test for ammonia is not applicable in the presence of arsenite. Arsenite is reduced by alkaline reducing agents to arsine, which blackens mercurous nitrate paper.

Cyanides, thiocyanates, ferro- and ferri-cyanides also yield ammonia under these experimental conditions; if these are present, or are suspected as a result of the preliminary tests, particularly that with concentrated sulphuric acid, they must first be removed as follows. Treat the *prepared* solution (sodium carbonate extract) with excess of nitrate-free silver sulphate, warm the mixture to about 60°, shake vigorously for 3–4 minutes, and filter from the silver salts of the interfering anions and excess of precipitant. Remove the excess of silver ions from the filtrate by adding an excess of sodium hydroxide solution and filter off the precipitated silver oxide. Evaporate the filtrate to about half bulk and test with zinc, aluminium or Devarda's alloy.

Test (ix). Borate test.—Make a paste of the original substance with calcium fluoride and concentrated sulphuric acid. Hold some of this in a platinum loop just outside the bottom of the Bunsen flame. A green flame, due to boron trifluoride, indicates borates. Barium and copper do not interfere when the test is carried out in the above manner.

Alternatively, the following test (which is strongly recommended) may be employed. Fit up the apparatus shown in Fig. 47, using rubber stoppers; the end of the right-angled bend should be drawn out into a capillary of not more than 0·5 mm. bore and 3–4 cm. long. The empty test-tube acts as a trap between the mouth and the test-tube containing the solution under test to prevent the solution from reaching the mouth should the capillary become blocked.

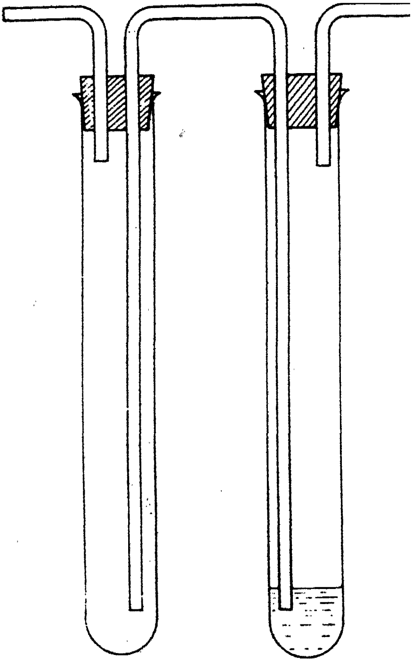

Fig. 47.

Place about 0·2 gram of the substance in the test-tube, add 1–2 c.c. of concentrated sulphuric acid with the aid of a dropper or small pipette, followed by 5–6 c.c. of methyl alcohol in 1 c.c. portions (caution !). Introduce the modified " wash-bottle " tubes and connect by a short length of rubber tubing to the trap. Blow gently through the liquid and direct the vapours issuing from the capillary into a colourless Bunsen flame. If a borate is present, the flame will acquire a characteristic green colour due to the volatile methyl borate $B(OCH_3)_3$. Under these experimental conditions copper and barium, which colour the flame green, do not interfere.*

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* This procedure is simpler than that of Section **IV, 44,** *14* ; the latter, however, is fool-proof and perfectly unambiguous.

EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

V,4. (A) PREPARATION OF A SOLUTION OF THE SOLID

Use small quantities of the powdered solid and examine the solubility in the following solvents in the order given: (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid, and (6) aqua regia. Try the solubility first in the cold and then on warming ; if in doubt whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass. If the substance dissolves in water, proceed immediately to test for the metal ions. If the use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I ; the precipitate may either be filtered off and examined for this group, or else the original substance may be dissolved in dilute nitric acid. If concentrated hydrochloric acid is employed for solution, it will be necessary to evaporate off most of the acid since certain metals of Group II (*e.g.*, cadmium) are not completely precipitated in the presence of large concentrations of acid. Where nitric acid has been used for the process of solution, all of the acid must be removed by evaporating nearly to dryness, adding a little hydrochloric acid, evaporating again to a small bulk, and then diluting with water ; these remarks also apply to aqua regia. For this reason nitric acid is often omitted from the solvents, and the tests confined to solvents 1, 2, 3 and 6.

When a suitable solvent has been found, the solution for analysis is prepared with 0·5–1 gram of the solid ; the volume of the final solution should be 20–25 c.c.

If the substance is insoluble in aqua regia (and in concentrated acids), it is regarded as *insoluble* and is treated by the special methods detailed in Section **V, 21** below.

V, 5. (B) GENERAL SCHEME FOR THE SEPARATION OF THE METALS INTO GROUPS

Before describing the general scheme for the separation of the metal ions into groups, the following facts are brought to the notice of the student as it is believed that by their proper understanding and appreciation, many of the usual pitfalls will be avoided.

(1) The analysis should not be conducted with large quantities of the substance because much time will be spent in filtering the precipitates and difficulty will be experienced in washing and dissolving them. It is therefore recommended that 0·5–1 gram should be employed for the analysis. After a little experience the student will be able to judge from the relative sizes of the precipitates, the relative quantities of the various components present in the mixture.

(2) The tests must, in the first place, be carried out in the order given. A group reagent will separate its particular group only from those which follow it and not from those which precede it. Thus hydrogen sulphide in the presence of dilute hydrochloric acid will separate Group II from Groups IIIA, IIIB, IV and V, but does not separate Group II from Group I. It is most important therefore that one group should be completely precipitated before precipitation of the next group is attempted, otherwise the group precipitates will be contaminated by metals from the preceding groups, and misleading results will be obtained.

Table XXIV.—Separation of Metals into Groups

(*Organic Acids, Boric, Hydrofluoric, Silicic and Phosphoric Acids being Present*)

<table>
<tr><td colspan="6">Add a few drops of dilute HCl to the cold solution. If a ppt. forms, continue adding dilute HCl until no further precipitation takes place. Filter (1).</td></tr>
<tr><td rowspan="5">Residue.
White.
Group I present.
Examine by Group Separation Table XXVII.</td><td colspan="5">Filtrate. Heat nearly to boiling, and saturate with H_2S (2). Filter.</td></tr>
<tr><td rowspan="4">Residue.
Coloured.
Group II present.
Examine by Group Separation Table XXVIII.</td><td colspan="4">Filtrate. Boil until H_2S is completely removed (test with lead acetate paper). Add 3–4 c.c. of concentrated HNO_3 (3), evaporate to dryness (4), moisten with a little concentrated nitric acid and heat gently; this will remove organic acids. If borates and fluorides (5) are present, the residue must be evaporated repeatedly with concentrated HCl. Add about 15 c.c. of dilute HCl to the residue and filter from any residue of silica, originating from any silicate present (6). Test a small portion (1 c.c.) of the solution for phosphate by adding it to 5 c.c. of ammonium molybdate solution and a few drops of concentrated nitric acid and warming to about 40°; a yellow ppt. shows phosphate is present. If phosphate is present, use the modified table (Table XXV) from this point (7).
If phosphate is absent, add 1–2 grams of solid NH_4Cl, heat to boiling, and add a slight excess of NH_4OH solution (<i>i.e.</i>, until the odour of ammonia is permanent) to the boiling solution. Filter.</td></tr>
<tr><td rowspan="3">Residue.
Group IIIA present.
Examine by Group Separation Table XXXIII.
[Some CaF_2 may also be precipitated here.]</td><td colspan="3">Filtrate. EITHER add a little more NH_4OH solution, warm and pass H_2S until precipitation is complete (usually 1 minute) OR add ammonium sulphide solution drop by drop to the hot solution until precipitation is complete (8). Filter.</td></tr>
<tr><td rowspan="2">Residue.
Group IIIB present.
Examine by Group Separation Table XXXIV.</td><td colspan="2">†Filtrate (9). Concentrate to about 10 c.c. in an evaporating basin (10), add a little NH_4Cl solution, a little NH_4OH solution, and then about 15 c.c. of $(NH_4)_2CO_3$ solution, warm (but do not boil), and filter (11).</td></tr>
<tr><td>Residue.
Group IV present.
Examine by Group Separation Table XXXV.</td><td>Filtrate (12). Divide into 2 unequal parts. Evaporate the smaller portion to dryness in the fume chamber until all ammonium salts are volatilised. Residue indicates Group V present. Examine by Group Separation Table XXXVII.</td></tr>
</table>

(3) The conditions for precipitation and for solution must be rigidly followed.

(4) All precipitates must be washed to remove adhering solution in order to avoid contamination by the metals remaining in the filtrate. The first washings should be added to the solution from which the precipitate has been filtered; later washings may be discarded.

(5) If the volume of the solution at any stage of the analysis becomes too large, it should be reduced by evaporation.

(6) All the apparatus employed in the analysis must be scrupulously clean. The use of dirty apparatus may be sufficient to introduce impurities into the substance under examination.

NOTES ON TABLE XXIV

(1) If the original solution was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear whilst hot, but $PbCl_2$ is deposited on cooling the solution. Any lead missed in this group will be precipitated with H_2S in Group II.

A precipitate may form upon the addition of HCl to certain neutral or slightly acid solutions even when none of the Group I metals are present. This may occur under the following conditions:—

(*a*) Aqueous solutions of Sb, Bi and Sn, not containing free HCl, precipitate as the oxychlorides upon the addition of this acid. The precipitate dissolves, however, upon the addition of excess of acid.

(*b*) Concentrated solutions of certain chlorides, *e.g.*, NaCl and $BaCl_2$, may form precipitates upon the addition of HCl; these dissolve on diluting with water.

(*c*) Borates may yield a white crystalline precipitate of boric acid, particularly if the acid is concentrated; only partial precipitation may occur here.

(*d*) Silicates may yield a gelatinous precipitate of silicic acid; only partial precipitation may occur here.

(*e*) The thio-salts of arsenic, antimony and tin will give the corresponding sulphides.

(2) The solution is contained in a small conical or round-bottomed flask (one of 50 c.c. capacity is suitable), fitted with a two-holed rubber stopper carrying two right-angled glass tubes, one of which reaches almost to the bottom of the flask and the other just below the stopper, as in Fig. 11(*c*); for further details see p. 116. The solution is heated to boiling and H_2S passed in for 2–3 minutes or until precipitation ceases; this can only be detected by filtering

a portion of the solution and testing the filtrate with H_2S. The use of a closed flask is much more economical and efficient than the crude method, often used by beginners, of passing the gas into the solution contained in an open test-tube.

It is important that the concentration of the acid (HCl) should be approximately correct, *i.e.*, 0·25–0·3*M*. This can be secured either by evaporation of the solution almost to dryness and then adding 2·5 c.c. of hydrochloric acid (1 part of concentrated acid : 1 part of water) and diluting to 50 c.c., or, more simply, by making use of the indicator, methyl violet (0·1% aqueous solution). The solution should give a blue-green to yellow-green colour (*p*H *ca.* 0·5) when about 0·5 c.c. is mixed with a minute drop of methyl violet solution upon a white porcelain tile. If the indicator turns yellow, it is too acid, and Pb, Cd and Sn may be incompletely precipitated (see Section **I, 16**). If too little acid is present (indicator blue or violet), Bi and Sb will not remain in solution, and Zn, Ni and Co may be precipitated with H_2S (see *Note 2* to Table SMI).

If an oxidising agent is present (*e.g.*, a permanganate, dichromate or ferric salt) as is shown by the gradual separation of a fine white precipitate of sulphur and/or a change of colour of the solution, it is usual to pass SO_2 into the hot solution until reduction is complete, then to boil off the excess of SO_2 (test with potassium dichromate paper) and finally to pass H_2S. Arsenates, in particular, are slowly precipitated by H_2S ; they are therefore also usually reduced by SO_2 to arsenites and then precipitated as As_2S_3 with H_2S, after removing the excess of SO_2 in order to avoid interaction of the latter with the H_2S and consequent separation of S. Stannic compounds may be partially reduced to the stannous state by this treatment ; the original solution or substance must be tested for the state of the arsenic or tin.

The objection to the use of SO_2 is that some sulphuric acid may be formed, particularly on boiling, and this may partially precipitate Pb, Sr and Ba as sulphates. Any precipitate formed in this process should therefore be examined for these cations ; $PbSO_4$ is soluble in ammonium acetate solution. An alternative procedure, which does not possess this disadvantage and is perhaps more expeditious, is to add 5 c.c. of dilute HCl and either 5 c.c. of rectified spirit or 2–3 c.c. of 10% formaldehyde solution, boil until reduction is complete, evaporate nearly to dryness (1–2 c.c.), dilute with water to about 15 c.c., and bring the solution to the proper acidity as described above. H_2S may then be passed into the resultant solution.

$$2KMnO_4 + 6HCl + 5H.CHO = 2KCl + 2MnCl_2 + 5H.CO_2H + 3H_2O.$$

$$K_2Cr_2O_7 + 8HCl + 5H.CHO = 2KCl + 2CrCl_3 + 5H.CO_2H + 4H_2O.$$

An arsenate may be reduced to arsenite by adding 1 c.c. of 10% NH_4I solution and 4 c.c. of concentrated HCl to the neutral solution, heating to boiling, and passing H_2S into the boiling solution until precipitation is complete (5–10 minutes) (see Section **III, 12,** reaction *1* ; **IV, 44,** *10*).

(3) Nitric acid is added to oxidise iron, if present, to the ferric state ; if originally present, it will have been reduced by the H_2S. Ferrous iron is incompletely precipitated by NH_4OH solution.

(4) Organic acids interfere with normal course of analysis. Thus in the presence of oxalic, tartaric or citric acids, the addition of the group reagent, NH_4Cl and NH_4OH solution, might fail to cause the precipitation of the hydroxides of Fe, Cr and Al. Furthermore, if oxalic acid is present, the oxalates of some of the metals of Groups IIIB, IV and of Mg, which are insoluble in ammoniacal solution, might be precipitated at this stage. It is therefore essential to destroy the organic acids, the presence of which has been indicated in the preliminary tests, before precipitation of Group IIIA. This is best effected by evaporation with concentrated nitric acid until the black residue is completely oxidised. It is important not to heat the residue too strongly as it may convert any Fe, Al or Cr present into the form of the sesquioxide which is difficultly soluble in concentrated HCl.

(5) Borates and fluorides of the metals of Groups IIIB, IV and of Mg are insoluble, and are therefore liable to be precipitated at this stage. They are most simply removed by repeated evaporation with concentrated HCl ; the boric acid will slowly volatilise with the steam and the hydrogen fluoride with the excess of HCl.

Alternatively, most of the boric acid may be removed by evaporating the filtrate from Group II to a small volume, adding 10 c.c. of concentrated hydrochloric acid and 5 c.c. of methyl alcohol, and continuing the evaporation just to dryness.

(6) Unless silicates are removed here, they are likely to be confused with $Al(OH)_3$ in the group separation. Repeated evaporation with concentrated HCl converts silicates into a granular form of silica, which is readily filtered.

Solutions of silicates are decomposed by dilute HCl into silicic acid, which may partially separate in Group I in the gelatinous form. That not precipitated in Group I will be precipitated by NH_4Cl solution in Group IIIA (see under Silicates, Section **IV, 26,** reaction 2).

(7) The phosphates of the metals of Groups IIIA, IIIB, IV and of Mg are insoluble in water and in ammoniacal solution, and may be precipitated at this stage. One method for the removal of phosphates is given in Table XXV.

(8) It is recommended that a small portion of the filtrate from Group IIIA be first tested with ammonium sulphide solution, or with NH_4OH solution and H_2S. If a precipitate is obtained, the main solution should be treated in this manner. If there is no precipitate, metals of Group IIIB are absent, and the main filtrate should be tested for Group IV metals.

The student should remember that conditions for the precipitation of Group IIIB differ from those in Group II. In the latter group, H_2S is passed into an acid solution in which the gas is only slightly soluble and hence much of it escapes unabsorbed. In the former group, the solution is alkaline and therefore the H_2S is readily absorbed. Moreover, if too much H_2S is employed, NiS may partially form a colloidal solution. This is avoided by passing H_2S for 0·5–1 minute, filtering, and testing for completeness of precipitation.

(9) If the solution or the filtrate from Group IIIB is brown or dark in colour, Ni may be suspected. The dark-coloured solution contains colloidal NiS and runs through the filter paper. In such a case, the solution is either boiled alone, or better, after neutralising with acetic acid, until the NiS is coagulated. This may be either added to the Group IIIB precipitate or tested separately for Ni.

(10) It is preferable to acidify immediately with acetic acid and then to concentrate to about 10 c.c. The excess of H_2S is thus rapidly removed, and the danger of oxidation of the ammonium sulphide on exposure to air to ammonium sulphate, and the consequent precipitation of the alkaline earth sulphates, is avoided. Another reason for immediate acidification is that absorption of CO_2 from the air with the formation of carbonate is prevented.

(11) The " ammonium carbonate solution " consists largely of ammonium bicarbonate NH_4HCO_3, and will accordingly form soluble bicarbonates with the alkaline earth metals unless excess of ammonium hydroxide is present, when the quantity of the normal carbonate $(NH_4)_2CO_3$ present will be increased. When precipitating Group IV, the solution should be warm to decompose any bicarbonates but must not be boiled, because the reaction, *e.g.*, $SrCO_3 + 2NH_4Cl \rightleftharpoons SrCl_2 + (NH_4)_2CO_3$, is reversible ; boiling will volatilise the $(NH_4)_2CO_3$, the reaction will proceed from left to right, and the precipitate will dissolve.

(12) It is recommended that 2 c.c. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solution be added, the resultant solution heated to boiling and allowed to stand for 5 minutes ; any precipitate which forms should be filtered off and discarded. This procedure ensures the complete removal of Group IV metals.

NOTES ON PHOSPHATE SEPARATION TABLE (TABLE XXV)

(1) The method described is usually known as the " basic acetate " method. It depends upon the insolubility of the phosphates of the metals of Group IIIA in dilute acetic acid as compared with the appreciable solubility of the phosphates of the metals of

V, 7. Table XXV.—Phosphate Separation Table

If a phosphate has been found in the General Table (XXIV) in the filtrate from Group II, add an equal bulk of NH_4Cl solution (or 1–2 grams of solid NH_4Cl), boil, add a slight excess of NH_4OH solution, and filter.

<table>
<tr><td rowspan="4">Filtrate. Test if free from phosphate by the ammonium molybdate test. Test for Groups IV and V as indicated in Table XXIV, or combine with filtrate marked with a dagger in that Table.</td><td colspan="4">Residue. May contain hydroxides of Fe, Al and Cr, and phosphates of Group IIIA, IIIB and IV metals and of Mg. Dissolve the ppt. in the <i>minimum</i> volume of warm dilute HCl. Test 1 c.c. for Fe with $K_4[Fe(CN)_6]$ solution. To the remainder of the <i>cold</i> solution, add dilute NH_4OH solution drop by drop until a faint permanent ppt. is just obtained (<i>i.e.</i>, which does not redisolve on shaking), add 2–3 c.c. of 50% acetic acid and 3–4 c.c. of saturated ammonium acetate solution, and boil. If a precipitate forms, add ammonium acetate solution until precipitation appears complete (1), boil and filter. Wash ppt.</td></tr>
<tr><td rowspan="3">Residue. Group IIIA present. Examine by Group Separation Table XXXIII.</td><td colspan="3">Filtrate. Add a neutral solution of $FeCl_3$ (2) drop by drop, shaking after each addition, until the solution is just red, indicating that the phosphate has been completely precipitated as $FePO_4$ and the slight excess of ferric chloride has been converted into colloidal basic ferric acetate (or into ferric acetate). Dilute to 150 c.c., boil for 2–3 minutes, and filter hot (3).
If the solution becomes red when ammonium acetate solution is added, there is enough iron present to combine with all the phosphoric acid; dilute to 150 c.c., boil for 2–3 minutes, and filter hot.</td></tr>
<tr><td rowspan="2">Residue. $FePO_4$ and some basic ferric acetate. Reject.</td><td colspan="2">Filtrate. Concentrate to 20–30 c.c., add 0·5 gram of NH_4Cl, and NH_4OH solution in slight excess. Filter, if necessary.</td></tr>
<tr><td>Residue. (4) Examine for Al and Cr (and Mn), if not previously tested for.</td><td>Filtrate. Examine for Groups IIIB, IV and V as given in General Table XXIV.</td></tr>
</table>

the later groups. The Fe, Al and Cr phosphates are precipitated in acetic acid solution (the precipitate may be contaminated with the basic acetates of these metals produced on boiling, and also with $Cr(OH)_3$), and the phosphate in the filtrate removed as $FePO_4$ by the addition of a slight excess of $FeCl_3$ solution. The Group IIIA precipitate is analysed in the usual way; the phosphate does not interfere with the ordinary separations and tests with the exception of the "aluminon" confirmatory test for aluminium.

(2) A "neutral" solution of $FeCl_3$ is prepared by dissolving the salt in water without using free HCl, and filtering the solution.

Alternatively, the method described in the foot-note to *test 6* in Section **VIII, 2** may be used.

(3) In a modification of this procedure, which is largely employed, the addition of ammonium acetate solution and acetic acid and of $FeCl_3$ solution is carried out in one operation. Use is then made of the facts: (*a*) $FePO_4$, $AlPO_4$ and $CrPO_4$ are insoluble in dilute acetic acid; (*b*) if a solution of ferric acetate is largely diluted and boiled, the iron is quantitatively precipitated as the basic acetate, $Fe(OH)_2.C_2H_3O_2$, and any Al and Cr present are simultaneously precipitated as phosphates and basic acetates (see, however, Section **VI, 2**). Hence Al and Cr are precipitated at the same time as the phosphate is removed as $FePO_4$ (for further details, see Chapter VI). The modified procedure is as follows:

Dissolve the ppt. in the minimum volume of dilute HCl. Test 1 c.c. for iron with $K_4[Fe(CN)_6]$ or NH_4CNS solution. To the remainder of the cold solution, add dilute NH_4OH solution drop by drop until a faint permanent ppt. is just obtained, add 2–3 c.c. of dilute acetic acid, and 3–4 c.c. of saturated ammonium acetate solution.

If the solution is now red in colour, it contains more than enough ferric iron to be equivalent to the phosphate present; the red colour is due to ferric acetate $Fe(C_2H_3O_2)_3$. Dilute to 150 c.c., boil for 2–3 minutes, filter, and wash with hot water.

If the solution is not red in colour, add "neutral" $FeCl_3$ solution drop by drop until the solution is red. Dilute to 150 c.c., boil for 2–3 minutes and filter hot.

<table>
<tr><td rowspan="2">Residue. Contains basic acetates and phosphates of Fe, Al and Cr. Test residue for Al and Cr by Group Separation Table XXXIII.</td><td colspan="2">Filtrate. Concentrate to 20–30 c.c., add 0·5 gram of NH_4Cl, and NH_4OH solution in slight excess. Filter, if necessary.</td></tr>
<tr><td>Residue. (4) Examine for Al and Cr (and Mn), if not previously tested for.</td><td>Filtrate. Examine for Groups IIIB, IV and V as in General Table XXIV.</td></tr>
</table>

(4) In general, no precipitate should be obtained here. If a precipitate is obtained, it should be examined for Al and Cr (and Mn), if not previously found.

NOTES ON TABLE XXVI (SIMPLIFIED GENERAL TABLE FOR SEPARATION OF METALS INTO GROUPS)

This table is intended for beginners and in consequence the various operations are given in somewhat greater detail than in Table XXIV.

(1) If the substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear while hot, but $PbCl_2$ is deposited

Table XXVI.—Separation of Metals into Groups

(Organic Acids, Boric, Hydrofluoric, Silicic and Phosphoric Acids being Absent)

<table>
<tr><td colspan="6">Add a few drops of dilute HCl to the cold solution. If a ppt. forms, continue adding dilute HCl until no further precipitation takes place. Filter (1).</td></tr>
<tr><td rowspan="5">Residue.
The ppt. may contain :—
$PbCl_2$—white.
Hg_2Cl_2—white.
AgCl—white.
Group I (Silver Group) present.
Examine by Group Separation Table XVII.</td><td colspan="5">Filtrate. This must give no further ppt. with a few drops of dilute HCl. Heat nearly to boiling and pass H_2S through the solution until precipitation is complete (2). Filter.</td></tr>
<tr><td rowspan="4">Residue. The ppt. may contain :—
HgS—black.
PbS—black.
Bi_2S_3—black*.
CuS—black.
CdS—yellow.
SnS—brown.
SnS_2—yellow.
Sb_2S_3—orange.
As_2S_3—yellow.
Groups IIA and IIB (Copper and Arsenic Groups) present.
Examine by Group Separation Tables XVIII and XIX.</td><td colspan="4">Filtrate. Dilute with one third volume of water and pass H_2S again ; add any ppt. which separates to that previously formed (3). Boil off H_2S (test with lead acetate paper) in a porcelain dish. Add 1 c.c. of concentrated HNO_3 and boil to oxidise any ferrous salts to the ferric state (4). Add 1–2 grams of solid NH_4Cl (or an equal volume of NH_4Cl solution), boil, add NH_4OH solution in slight excess, boil and filter immediately.</td></tr>
<tr><td rowspan="3">Residue. The ppt. may contain :—
$Fe(OH)_3$—reddish-brown.
$Cr(OH)_3$—green.
$Al(OH)_3$—white.
Possibly MnO_2,H_2O—brown.
Group IIIA (Iron Group) present.
Examine by Group Separation Table XX.</td><td colspan="3">Filtrate. Add ammonium sulphide solution drop by drop until precipitation is complete (or add 1–2 c.c. NH_4OH solution and pass H_2S for 1 minute) (6). Boil and filter.</td></tr>
<tr><td rowspan="2">Residue.
The ppt. may contain :—
CoS—black.
NiS—black.
MnS—pink.
ZnS—white.
Group IIIB (Zinc Group) present.
Examine by Group Separation Table XXI.</td><td colspan="2">Filtrate. This must give no further ppt. with ammonium sulphide solution (or H_2S) (6). Concentrate to about 10 c.c. in a porcelain dish. Add a little NH_4OH solution, then $(NH_4)_2CO_3$ solution in slight excess., Warm, but do not boil. Allow to stand 5 minutes and filter.</td></tr>
<tr><td>Residue. The ppt. may contain :—
$BaCO_3$—<i>white</i>.
$SrCO_3$—white.
$CaCO_3$—white.
Group IV (Calcium Group) present.
Examine by Group Separation Table XXII.</td><td>Filtrate. May contain Mg^{++}, Na^+ and K^+ (7). Divide into 2 unequal parts. Evaporate smaller portion to dryness in the fume cupboard until all ammonium salts volatilised. White residue.
Group V (Alkali Group) present.
Examine by Group Separation Table XXIII.</td></tr>
</table>

* Sometimes dark-brown.

on cooling the solution, due to the slight solubility of the salt in cold water. Lead may be found in Group II, even if it is not precipitated in Group I.

(2) For details of the passage of H_2S through the solution, see note 2 to Table XXIV.

If arsenates (or dichromates or permanganates) are suspected, pass SO_2 into the solution for several minutes, boil off the excess of SO_2, and then pass H_2S.

Before passing H_2S, the acidity of the solution should be adjusted. This may be done by evaporation of the solution almost to dryness and adding 2·5 c.c. of hydrochloric acid (1 part of concentrated acid : 1 part of water) and diluting to 50 c.c. Another method is to make use of the indicator, brilliant cresyl blue ; details will be found in note 2 to Table XXIV.

(3) This is really unnecessary if the acidity of the solution has been adequately adjusted. It is, however, a useful precaution for beginners, since CdS, PbS and SnS are incompletely precipitated in the presence of much HCl.

(4) If iron was originally present in the ferric state, it will be reduced to the ferrous state by H_2S. It must be oxidised to the ferric condition in order to ensure complete precipitation with NH_4Cl and NH_4OH solution. The original solution must be tested to determine whether the iron is present in the ferrous or ferric condition.

(5) In the presence of excess of NH_4Cl, NH_4OH solution causes little or no precipitation of Mn. A certain amount of the Mn exists in solution as $Mn(OH)_2$. On exposure to the atmosphere, some of the $Mn(OH)_2$ may be oxidised to an insoluble compound (MnO_2,H_2O or amphoteric manganous acid H_2MnO_3 or $MnO(OH)_2$), and this is precipitated with the hydroxides of the Group IIIA metals. It is therefore important to filter immediately after the addition of the NH_4OH solution.

(6) If a brown solution or dark-coloured filtrate is obtained, Ni may be suspected. The dark-coloured solution contains NiS, which runs through the filter paper. In such a case, the solution is either boiled alone (adding water, if necessary, to prevent evaporation to dryness) or better, boiled, after neutralising with acetic acid, until the NiS is coagulated. This may either be added to the Group IIIB precipitate or tested separately for Ni.

(7) It is best to add 2–3 c.c. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solution to precipitate any of the Group IV metals which may be present, removing these by filtration, and then evaporating to dryness.

Beginners may use Tables XVII–XXIII for the analysis of the various group precipitates, particularly in the analysis of single salts or simple mixtures. When some experience has been gained, Tables XXVII–XXXVII may be employed.

Explanation (Table XXVII)

The metal ions of lead, silver and mercurous mercury are precipitated by dilute HCl as the insoluble chlorides $PbCl_2$, AgCl and Hg_2Cl_2 respectively; the chlorides of all the other common metals are soluble. The separation of these is based upon the following facts:—

(1) $PbCl_2$ is soluble in boiling water, whilst Hg_2Cl_2 and AgCl are insoluble. Extraction of the precipitate with hot water therefore removes the $PbCl_2$. Confirmatory tests for lead ions are applied to the solution so obtained, *e.g.*,

$$PbCl_2 + K_2CrO_4 = PbCrO_4 + 2KCl, \text{ etc.,}$$

(for details, see under Lead, Section **III**, 2).

(2) AgCl is soluble in dilute NH_4OH solution, yielding the soluble complex salt $[Ag(NH_3)_2]Cl$. The solution of this complex salt is decomposed by both dilute HNO_3 and by KI solution with the precipitation of the insoluble salts AgCl and AgI respectively.

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl;$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl + 2NH_4NO_3;$$

$$[Ag(NH_3)_2]Cl + KI + 2H_2O = AgI + KCl + 2NH_4OH.$$

[*continued on p.* 362

V, 9. Table XXVII.—Analysis of Group I (Silver Group)

<table>
<tr><td colspan="3">The ppt. may consist of $PbCl_2$, AgCl and Hg_2Cl_2. Wash the ppt. on the filter first with dilute HCl, then 2–3 times with <i>small</i> amounts of <i>cold</i> water, and reject the washings. Transfer the ppt. to a boiling tube or to a small beaker, and boil with 15–20 c.c. of water. Filter hot.</td></tr>
<tr><td colspan="2">Residue. May contain Hg_2Cl_2 and AgCl. Wash the ppt. several times with hot water until the washings give no ppt. with K_2CrO_4 solution ; this ensures the complete removal of the Pb.
Pour 10–15 c.c. of warm NH_4OH solution (1 : 1) over the ppt. and collect the filtrate.</td>
<td rowspan="2">Filtrate. May contain $PbCl_2$. Cool the solution, when a white crystalline ppt. of $PbCl_2$ will be obtained if Pb is present in any quantity. Divide filtrate into 3 parts :
(i) Add K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$, insoluble in dilute acetic acid.
(ii) Add KI solution. Yellow ppt. of PbI_2, soluble in boiling water to a colourless solution, which deposits beautiful yellow crystals on cooling.
(iii) Add dilute H_2SO_4. White ppt. of $PbSO_4$, soluble in ammonium acetate solution.
Pb present.</td></tr>
<tr><td>Residue. If black, consists of $Hg(NH_2)Cl$ + Hg.
Hg(ous) present.[*]</td>
<td>Filtrate.[‡] May contain $[Ag(NH_3)_2]Cl$. (If not clear, pour through filter again.)
Divide into 2 parts :
(i) Add dilute HNO_3 until acid (shake solution, and test with litmus). White ppt. of AgCl.
(ii) Add a few drops of KI solution.
Pale-yellow ppt. of AgI.
Ag present.</td></tr>
</table>

(3) The conversion of Hg_2Cl_2 by dilute NH_4OH solution into the insoluble black mixture of amino mercuric chloride $Hg(NH_2)Cl$ and finely divided mercury.

$$Hg_2Cl_2 + 2NH_4OH = Hg(NH_2)Cl + Hg + NH_4Cl + 2H_2O.$$

Aqua regia converts the black mixture into $HgCl_2$ (see under

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[*] This is a conclusive test for mercurous mercury. It may be further confirmed by dissolving the ppt. in 3–4 c.c. of boiling aqua regia, diluting, filtering if necessary, and then adding $SnCl_2$ solution. A white ppt. (Hg_2Cl_2), turning grey (Hg), is obtained.

[‡] If Hg is present in reasonably large quantity and Ag has not been detected, carry out the above confirmatory test for Hg, and treat the thoroughly washed residue, insoluble in aqua regia, with dilute NH_4OH solution. Filter, if necessary, and add dilute HNO_3 to the clear solution. A white ppt. of AgCl will form if small amounts of Ag are present. This is an alternative procedure for separating Hg and Ag in the Hg_2Cl_2—AgCl mixture.

When the amount of $Hg(NH_2)Cl$ + Hg is large and that of AgCl is small, the latter may be reduced to metallic silver according to the reaction,

$$2Hg + 2AgCl = Hg_2Cl_2 + 2Ag,$$

and thus escape detection.

Mercury, Section **III, 8,** reaction *1*). The mercuric ion is then detected with $SnCl_2$ solution or, in the neutral solution, with the ethylenediamine reagent (Section **III, 8,** reaction *7*) :

$$2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2 ;$$
$$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg.$$

V,10. Table XXVIII.—Analysis of Group II (Copper and Arsenic Groups). Separation of Group IIA (Copper Group) and Group IIB (Arsenic Group)

The ppt. may consist of the sulphides of the Group IIA metals (HgS, PbS, Bi_2S_3, CuS, CdS) and those of Group IIB (As_2S_3, Sb_2S_3, Sb_2S_5, SnS, SnS_2). Wash the precipitated sulphides with a little H_2S water[*] (the latter to prevent conversion of CuS into $CuSO_4$ by atmospheric oxidation), transfer to a porcelain dish, add about 10 c.c. of *yellow* ammonium sulphide solution, heat to 50–60° [§], and maintain at this temperature for 3–4 minutes with constant stirring. Filter [‡].

Residue. May contain HgS, PbS, Bi_2S_3, CuS, CdS. Wash once or twice with small quantities of ammonium sulphide solution, then with 1% NH_4NO_3 solution, and reject all washings. **Group IIA present.**	**Filtrate.** May contain solutions of the thio-salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. Just acidify by adding concentrated HCl drop by drop (test with litmus paper), and warm gently. A yellow or orange ppt., which may contain As_2S_5, Sb_2S_5 and SnS_2, indicates **Group IIB present.**

Explanation

The sulphides of mercuric mercury, lead, bismuth, copper and cadmium and of arsenic, antimony and tin are precipitated by H_2S in the presence of dilute HCl. The sulphides of arsenic (As_2S_3), antimony (Sb_2S_3 and Sb_2S_5) and of tin (SnS_2) (Group IIB) are soluble in yellow ammonium sulphide solution forming thio-salts, whilst those of the other metals (Group IIA) are insoluble. Stannous sulphide SnS is insoluble and antimony trisulphide Sb_2S_3 is sparingly soluble in colourless ammonium sulphide solution, but both of these dissolve readily in the yellow ammonium sulphide solution; the SnS is converted into the thio-stannate. Colourless ammonium sulphide solution contains largely $(NH_4)_2S$ and some NH_4HS, whilst yellow ammonium sulphide solution contains an excess of sulphur and may be formulated $(NH_4)_2S_x$ (the formula $(NH_4)_2S_2$ is often used for the last-named in writing equations). For this reason yellow ammonium sulphide solution must always be employed for the separation of Groups IIA and IIB, especially if Sn is present.

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[*] It is recommended that about 5% by weight of NH_4Cl be added in order to inhibit the production of colloidal sulphides in the washing process.

[§] If the ammonium sulphide extract is boiled for some time in the air, a red antimony oxysulphide Sb_2OS_2 may be precipitated.

[‡] If the precipitate is completely soluble in yellow ammonium sulphide solution, Group IIA is absent.

$$As_2S_3 + 3(NH_4)_2S_2 = S + 2(NH_4)_3AsS_4$$ ammonium thio-arsenate.

$$Sb_2S_3 + 3(NH_4)_2S_2 = S + 2(NH_4)_3SbS_4$$ ammonium thio-antimonate.

$$SnS_2 + (NH_4)_2S_2 = S + (NH_4)_2SnS_3$$ ammonium thio-stannate.

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Upon acidifying the solutions of the thio-salts with dilute HCl, the sulphides are precipitated, and the excess of ammonium sulphide is decomposed.

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$
$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S.$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$
$$(NH_4)_2S_2 + 2HCl = S + 2NH_4Cl + H_2S.$$

‡ *Alternative Procedure for the Separation of Copper and Cadmium (See Table XXIX)*

Divide the solution into 2 unequal parts. Confirm Cu in the smaller portion with dilute acetic acid and $K_4[Fe(CN)_6]$ solution. Acidify the larger portion of the blue solution with dilute H_2SO_4, and add 5 c.c. in excess. Heat the resultant solution to boiling and remove from the flame. Add about 1 gram of iron filings or powder. When the reaction is over, allow the precipitated copper to settle; Cd remains in solution. Filter. Almost neutralise the filtrate with NH_4OH solution, and pass H_2S. A yellow precipitate (CdS) indicates Cd.

$$CuSO_4 + Fe = Cu + FeSO_4.$$
$$CdSO_4 + H_2S \rightleftharpoons CdS + H_2SO_4.$$

V, 11. Table XXIX.—Analysis of Group IIA (Copper Group)†

The ppt. may contain HgS, PbS, Bi_2S_3, CuS and CdS. Transfer to a beaker*, add 10–15 c.c. of dilute HNO_3, boil for 2–3 minutes, and filter.

Residue. Black; HgS. Dissolve in aqua regia or in Br_2 water, boil off the halogen, dilute and add $SnCl_2$ solution. White or grey ppt. Alternatively, add the ethylene-diamine reagent (Section **III, 3,** 7) Blue-violet ppt. **Hg(ic) present.**

Filtrate. May contain nitrates of Pb, Bi, Cu and Cd. Test a small portion for Pb by adding dilute H_2SO_4 and alcohol. A white ppt. of $PbSO_4$ indicates *Pb present.* If Pb present, add dilute H_2SO_4 to the remainder of the solution, concentrate in the fume cupboard until white fumes (from the dissociation of the H_2SO_4) appear. Cool, add 10–20 c.c. of water, stir, allow to stand 2–3 minutes, and filter.

Residue. White; $PbSO_4$. Wash. Dissolve in ammonium acetate solution, add dilute acetic acid and K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$. **Pb present.**

Filtrate. May contain nitrates and sulphates of Bi, Cu and Cd. Add NH_4OH solution until solution is distinctly alkaline. Filter.

Residue. White; $Bi(OH)_3$. Wash. Dissolve in the minimum volume of dilute HCl and pour into cold sodium stannite solution§. Black ppt. Alternatively, dissolve the ppt. in dilute HNO_3, and add Na_2HPO_4 solution. White ppt. of $BiPO_4$. **Bi present.**

Filtrate.

(i) If blue, contains $[Cu(NH_3)_4]SO_4$, and Cu indicated.

(ii) If colourless, Cu absent.

Confirm Cu by acidifying a portion of the filtrate with acetic acid and add $K_4[Fe(CN)_6]$ solution. Reddish-brown ppt.

Cu present.

To Test for Cd ‡

(i) *Filtrate blue.* Add KCN solution drop by drop until colour discharged, and add a further 1 c.c. in excess. Pass H_2S for 30 seconds. Immediate yellow ppt. of CdS.

Cd present.

(ii) *Filtrate colourless* (may contain $[Cd(NH_3)_4]SO_4$). Pass H_2 30 seconds. Immediate yellow ppt. of CdS.

Cd present.

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† For alternative Table, which is strongly recommended, see Section **III, 10,** Table XVIIIA.

* This is most easily effected by making a small hole in the filter with a pointed glass rod and washing the ppt. into the beaker with dilute HNO_3.

§ Sodium stannite solution is prepared by adding NaOH solution to 1 c.c. of $SnCl_2$ solution until the ppt. of $Sn(OH)_2$ first formed redissolves.

‡ *For note, see p. 364*

Explanation

The residue insoluble in yellow ammonium sulphide solution may contain HgS, PbS, Bi_2S_3, CuS and CdS. Their separation is based upon the following facts :—

(1) HgS is insoluble in dilute HNO_3 ; the sulphides of Pb, Bi, Cu and Cd dissolve with the formation of nitrates.

$$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O.$$

$$Bi_2S_3 + 8HNO_3 = 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O.$$

One confirmatory test for Hg involves the conversion of the HgS by aqua regia into $HgCl_2$, and the familiar reduction of the latter by $SnCl_2$ solution*.

$$3HgS + 2HNO_3 + 6HCl = 3HgCl_2 + 3S + 2NO + 4H_2O.$$

(2) The filtrate from the nitric acid treatment contains the nitrates of Pb, Bi, Cu and Cd. Dilute H_2SO_4 precipitates Pb as $PbSO_4$, leaving the other metals (which form soluble sulphates) in solution.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$

The object of the evaporation with H_2SO_4 until white fumes appear is to eliminate the HCl and HNO_3, which have a slight solvent action upon the $PbSO_4$. The $PbSO_4$ is converted by ammonium acetate solution into lead acetate, which is only feebly ionised in the presence of excess of acetate ions. The insoluble $PbCrO_4$ is precipitated upon the addition of K_2CrO_4 or $K_2Cr_2O_7$ solution.

$$PbSO_4 + 2NH_4.C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4.$$

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O$$
$$= 2PbCrO_4 + 2H.C_2H_3O_2 + 2K.C_2H_3O_2.$$

(3) The addition of *excess* of NH_4OH solution results in the precipitation of $Bi(OH)_3$ and the formation of the soluble complex salts, $[Cu(NH_3)_4]SO_4$ and $[Cd(NH_3)_4]SO_4$.

$$Bi_2(SO_4)_3 + 6NH_4OH = 2Bi(OH)_3 + 3(NH_4)_2SO_4.$$

$$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O.$$

$$CdSO_4 + 4NH_4OH = [Cd(NH_3)_4]SO_4 + 4H_2O.$$

The sodium stannite solution reduces the $Bi(OH)_3$ to Bi and is itself oxidised to sodium stannate.

$$2Bi(OH)_3 + 3Na_2[SnO_2] = 2Bi + 3Na_2[SnO_3] + 3H_2O.$$

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* Confirmatory tests will not, in general, be described in detail where they have already been given under the reactions of the metal ions.

(4) The addition of acetic acid to the blue solution decomposes the complex into $CuSO_4$ and $NH_4.C_2H_3O_2$; $K_4[Fe(CN)_6]$ solution yields reddish-brown $Cu_2[Fe(CN)_6]$.

$$[Cu(NH_3)_4]SO_4 + 4H.C_2H_3O_2 = CuSO_4 + 4NH_4.C_2H_3O_2.$$

$$K_4[Fe(CN)_6] + 2CuSO_4 = Cu_2[Fe(CN)_6] + 2K_2SO_4.$$

If copper is absent, passage of H_2S into the solution of the complex salt precipitates CdS, the final reaction being:

$$[Cd(NH_3)_4]SO_4 + H_2S + 2H_2O = CdS + (NH_4)_2SO_4 + 2NH_4OH.$$

If copper is present, the addition of excess of KCN solution converts the ammine complexes into the colourless complex cyanides, potassium cupr*o*cyanide $K_3[Cu(CN)_4]$ and potassium cadm*i*cyanide $K_2[Cd(CN)_4]$.

$$2[Cu(NH_3)_4]SO_4 + 10KCN + 8H_2O = 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2 + 8NH_4OH.$$

$$[Cd(NH_3)_4]SO_4 + 4KCN + 4H_2O = K_2[Cd(CN)_4] + K_2SO_4 + 4NH_4OH.$$

he cyanogen produced reacts with the NH_4OH solution:

$$(CN)_2 + 2NH_4OH = NH_4CNO + NH_4CN + H_2O^*.$$

With potassium cuprocyanide, the concentration of the cuprous ions produced by the secondary ionisation of the complex ion $[Cu(CN)_4]^{---}$ is insufficient to exceed the solubility product of Cu_2S upon the addition of H_2S; no precipitation therefore occurs. Potassium cadmicyanide, on the other hand, is relatively unstable (compare Section **I, 20**) and the concentration of cadmium ions arising from the secondary dissociation of the $[Cd(CN)_4]^{--}$ is sufficient to exceed the solubility product of CdS when H_2S is passed into the solution.

$$K_3[Cu(CN)_4] \rightleftharpoons 3K^+ + [Cu(CN)_4]^{-} \rightleftharpoons 3K^+ + Cu^+ + 4CN^-.$$

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{-} \rightleftharpoons 2K^+ + Cd^{++} + 4CN^-.$$

Explanation (*Table XXX*)

The ppt. obtained upon acidifying the ammonium sulphide extract may contain As_2S_5, Sb_2S_5, SnS_2 and S. Their separation depends upon:—

(1) As_2S_5 is almost unaffected by concentrated HCl, whilst Sb_2S_5 and SnS_2 dissolve forming chlorides.

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* Compare $Cl_2 + 2NaOH = NaOCl + NaCl + H_2O$.

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + 2S.$$

$$SnS_2 + 4HCl = SnCl_4 + 2H_2S.$$

In one confirmatory test for As, the ppt. of As_2S_5 is dissolved in $(NH_4)_2CO_3$ solution whereby a mixture of thioarsenates is produced; upon acidification of the solution, As_2S_5 is re-precipitated.

$$As_2S_5 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3CO_2.$$

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 3H_2S + 6NH_4Cl.$$

In the other test, the As_2S_5 is converted by means of HNO_3 into H_3AsO_4, and the latter into $Mg(NH_4)AsO_4$ with magnesia mixture and NH_4OH solution.

$$3As_2S_5 + 10HNO_3 + 4H_2O = 6H_3AsO_4 + 15S + 10NO.$$

$$H_3AsO_4 + 3NH_4OH + MgCl_2$$
$$= Mg(NH_4)AsO_4 + 2NH_4Cl + 3H_2O.$$

(2) The filtrate from the HCl treatment contains stannic chloride and antimony chloride. The addition of metallic iron to the diluted solution reduces the $SnCl_4$ to $SnCl_2$ first, and then the $SbCl_3$ to black Sb, which may be contaminated with C derived from the iron; upon filtration, the solution contains $SnCl_2$ and is free from Sb. The $SnCl_2$ is identified by the usual reaction with $HgCl_2$ solution; the $FeCl_2$ produced has no action upon the $HgCl_2$.

$$2SbCl_3 + 3Fe = 2Sb + 3FeCl_2.$$

$$SnCl_4 + Fe = SnCl_2 + FeCl_2.$$

(3) The addition of NH_4OH solution and excess of oxalic acid to the solution containing the antimony and tin chlorides results in the formation of a tin-oxalate complex ion, in which the tin is present in the anion. The antimony compound does not behave in this way, or at least the antimony-oxalate complex ion is unstable, and an appreciable concentration of antimony ions exist in solution. Hence when H_2S is passed into the solution, Sb_2S_3 alone is precipitated. Continued treatment with H_2S may, however, result in partial decomposition of the tin-oxalate complex ion; this will be indicated by the darkening of the orange Sb_2S_3 precipitate.

Explanation (Table XXXI)

In this method the separation of As_2S_5, Sb_2S_5 and SnS_2 is based upon the following facts :—

(1) The solubility of As_2S_5 in ammonium carbonate solu-

V,12. Table XXX.—Analysis of Group IIB (Arsenic Group)

Method A

The yellow ammonium sulphide extract of the Group II ppt. (see Table XXVIII) is treated with HCl, with constant stirring, until it is slightly acid (test with litmus paper), the solution warmed and shaken for 1–2 minutes. A yellow or orange ppt. indicates As, Sb and/or Sn present *. A fine white or yellow ppt. is sulphur only. Filter and wash the ppt., which may contain As_2S_5, Sb_2S_5, SnS_2 and S, with hot water; reject the washings.

Transfer the ppt. to a small conical flask, add 10 c.c. of concentrated HCl, and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2–3 c.c. of water, and filter.

Residue. Yellow; As_2S_5 (+ S). Wash with hot water. EITHER—Heat gently for 2–3 minutes with powdered ammonium carbonate. Filter, if necessary. Acidify with dilute HCl. Yellow ppt. of As_2S_5. **As present.** OR—Dissolve ppt. in concentrated HNO_3 or in concentrated HCl + a few crystals of $KClO_3$, evaporate off most of the acid, and add excess of NH_4OH solution. Filter, if necessary. Add magnesia solution and cool. Shake vigorously or rub the sides of the vessel with a glass rod if a ppt. does not appear immediately. White crystalline ppt. of $Mg(NH_4)AsO_4$. Dissolve ppt. in dilute HCl (1 : 1) and pass H_2S. Yellow ppt. of As_2S_3. **As present.**‡	**Filtrate.** May contain $SbCl_3$ (and/or $H[SbCl_4]$ and $SnCl_4$ (or $H_2[SnCl_6]$). Dilute with water to 15–20 c.c. Divide into 3 equal parts. (i) Add 1–2 grams of Fe powder or preferably 12 inches of thin iron wire, warm until a steady evolution of H_2 takes place, and allow reduction to proceed for 3–4 minutes. Filter into test-tube containing 2–3 c.c. of $HgCl_2$ solution. White ppt. (Hg_2Cl_2), turning grey (Hg) if solution contains considerable quantity of Sn. **Sn present.**‡ Two cases may arise:— (ii) **Tin is present.** To remaining 2/3 of solution contained in a small beaker, add NH_4OH solution until *just* alkaline, then 5–6 grams of oxalic acid and 50 c.c. of water. Boil until crystals dissolve, and pass H_2S through the hot solution for 3–4 minutes, but no longer. Orange ppt. of Sb_2S_3. **Sb present.** (iii) **Tin is absent.** Dilute remaining 2/3 of solution with 50 c.c. of water, and pass H_2S. Orange ppt. of Sb_2S_3. **Sb present.**

* If Cu is present in the original Group II ppt., a small amount may be dissolved by the ammonium sulphide solution and re-precipitate here (brownish-red).

‡ If As or Sn is found, the original solution must be tested to ascertain whether present in the *-ous* or *-ic* state.

tion ; Sb_2S_5 (or Sb_2S_3) is practically insoluble, and SnS_2 only slightly soluble in this reagent. The equations have been given in the Explanation of *Method A*.

The confirmatory test for As described here involves the dissolution of the As_2S_3 in NH_4OH solution with the formation of sulpho-salts ; these are oxidised by H_2O_2 to arsenate, which is tested for with magnesia mixture in the usual manner.

$$As_2S_3 + 6NH_4OH = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3H_2O.$$

$$(NH_4)_3AsS_4 + 8NH_4OH + 16H_2O_2$$
$$= (NH_4)_3AsO_4 + 4(NH_4)_2SO_4 + 20H_2O.$$

$$(NH_4)_3AsO_3S + 2NH_4OH + 4H_2O_2$$
$$= (NH_4)_3AsO_4 + (NH_4)_2SO_4 + 5H_2O.$$

(2) Sb_2S_5 and SnS_2 both dissolve in concentrated HCl forming solutions of the chlorides $SbCl_3$ (or $H[SbCl_4]$ or $H_2[SbCl_6]$) and $SnCl_4$ (or $H_2[SnCl_6]$). The detection of Sb in procedure *1* depends upon the displacement of the Sb by the Sn, which is deposited upon the silver as a black stain (actually a silver-tin couple is formed, which electrolyses the solution). In procedure *2*, a platinum-zinc couple is formed and Sb is deposited upon the platinum. In the presence of Zn, Sn is also deposited upon the zinc, so that if the residue is dissolved in concentrated HCl, the resultant solution contains $SnCl_2$, which is identified with $HgCl_2$ solution.

Table XXXI.—Analysis of Group IIB (Arsenic Group)

Method B

The ammonium sulphide solution extract (Table XXVIII) is treated with HCl with constant stirring until the solution is slightly acid (test with litmus paper). A yellow or orange ppt. indicates As, Sb and/or Sn present. A fine white or yellow ppt. is probably S and may be rejected. Filter and wash ppt.; reject washings. Transfer ppt. to a small beaker, add 5–10 c.c. of water and 3–4 grams of solid ammonium carbonate, and digest for about 5 minutes at 70° (best effected by heating on a water bath). Filter.

Residue. May contain Sb_2S_5, SnS_2 and S. Wash. Dissolve ppt. by warming with concentrated HCl (preferably in a small flask fitted with a reflux condenser). Filter, if necessary (residue is only S and traces of As_2S_3). Concentrate filtrate to about 2 c.c. Use procedure 1 or 2 in testing for Sb.

Procedure 1. Put 2–3 drops of the solution on the surface of a clean silver coin*. Allow to stand for 1–2 minutes to make certain that no colour develops from the action of the solution alone. Select a small V-shaped piece of tin foil, and place this so that one end dips into the solution and the other end touches the bare coin. A black stain of Sb will soon develop on the surface of the coin.

Sb present.

Procedure 2. Dilute the concentrated solution to about 10 c.c. Divide into two parts. Into one part introduce a clean piece of Pt foil. Place a piece of bright Zn in *contact* with the Pt and keep the two surfaces in contact for 3–4 minutes. A coal-black stain on the Pt after removing the Zn, insoluble in NaOCl solution, indicates

Sb present.

To the other portion of the diluted solution from procedure 2, or of the residue from procedure 1, diluted to about 5 c.c., add a small piece of Zn. Allow to stand for several minutes. Decant the clear solution. Dissolve residue in a little concentrated HCl; add $HgCl_2$ solution. White ppt. (Hg_2Cl_2), turning grey (Hg).

Sn present.

Filtrate. May contain $(NH_4)_3AsS_4$ and $(NH_4)_3AsO_3S$. Acidify with dilute HCl. Yellow ppt. of As_2S_3.

As present.

Confirm As by dissolving in concentrated HNO_3 and proceeding as described in *Method A*, or by dissolving ppt. in NH_4OH solution, and adding 1 c.c. of H_2O_2 (to oxidise to arsenate). Add magnesia mixture.

White crystalline ppt. of $Mg(NH_4)AsO_4$.

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* Cleaning is simply effected by moistening with HNO_3 and washing thoroughly.

Table XXXII.—Analysis of Group IIB (Arsenic Group)

Method C

The yellow ammonium sulphide extract (see Table XXVIII) is acidified with acetic acid, and the precipitation of the sulphides of As, Sb and Sn completed by passage of H_2S. The mixed sulphides are filtered off, washed with H_2S water and dissolved in dilute NaOH solution. H_2O_2 is then added (to oxidise any *-ous* compounds present to the *-ic* state), and the solution boiled for 15 minutes to destroy the excess of H_2O_2. The solution is acidified with HCl (use litmus or methyl red paper), and then 4 c.c. of concentrated HCl added in excess for each 50 c.c. of the solution. The resultant solution is cooled to 5° (preferably to 0°, in ice)* and excess of 0·5% aqueous cupferron solution, also cooled to 5° (or 0°)*, added in slight excess with vigorous stirring, which is continued for 2–3 minutes. Filter, and wash thoroughly with cupferron solution until free from chloride; reject the washings.

Residue. Yellowish-white; tin-cupferron complex salt.

Filtrate. Pass H_2S and filter. Reject filtrate.

Residue. May contain As_2S_5, Sb_2S_5 (or Sb_2S_3) and S. Transfer the ppt. to a small conical flask, add 10 c.c. of concentrated HCl, and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2–3 c.c. of water, and filter.

Residue. Yellow; As_2S_3 (+ S). Wash ppt. with hot water. Heat gently for 2–3 minutes with powdered ammonium carbonate. Filter, if necessary. Acidify with dilute HCl.

Yellow ppt. of As_2S_5.

As present.

Filtrate. May contain $SbCl_3$ (and/or $H[SbCl_4]$). Dilute to 50 c.c., and pass H_2S for several minutes.

Orange ppt. of Sb_2S_3.

Sb present.

Explanation

This method is based upon the following facts :—

(1) Stannous, stannic and antimonious compounds, in the presence of HCl, give yellowish-white to white precipitates with aqueous cupferron solution; antimonic, arsenious and arsenic compounds give no precipitate under these conditions. Hence if a solution containing Sn, Sb and As in the *-ic* states

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* Efficient cooling is essential in order to prevent the flocculent tin-cupferron compound from resinifying, when it is difficult to filter and wash thoroughly.

—this is assured by dissolving the precipitated sulphides in NaOH solution and oxidising with H_2O_2—is treated with cupferron solution, only the tin-cupferron complex separates.

(2) The theoretical basis for the separation of As_2S_5 and Sb_2S_5 (or Sb_2S_3) has been described in the explanation of *Method A*.

V,13. Table XXXIII.—Analysis of Group IIIA (Iron Group)*

The ppt. produced by adding NH_4Cl and NH_4OH solution may contain $Fe(OH)_3$, $Cr(OH)_{23}$, $Al(OH)_3$ (and MnO_2,xH_2O and CaF_2 which are often precipitated here). Wash it with hot 1% NH_4Cl solution (Co, Ni and Zn remain in solution as the complex ammine ions). Transfer the ppt. to an evaporating basin, and *either* add 15 c.c. of water and 1–1·5 grams of Na_2O_2 portion-wise (caution!) *or* add 10 c.c. of NaOH solution and 5 c.c. of 10 volume H_2O_2, boil the solution for 4–5 minutes (until O_2 ceases to be evolved). Dilute somewhat and filter.

Residue. May contain $Fe(OH)_3$ (reddish-brown), and possibly $MnO.(OH)_2$. Wash with hot water. Divide into 2 parts : (i) Dissolve in dilute H_2SO_4 (add a few drops of H_2O_2, if necessary). *Either* add a few drops of KCNS solution—red colouration, *or* add $K_4[Fe(CN)_6]$ solution—blue ppt. **Fe present.** The original solution or substance must be tested with $K_3[Fe(CN)_6]$ or KCNS solution to determine whether Fe^{++} or Fe^{+++}. (ii) Dissolve in 50% HNO_3. Add about 1 gram of Pb_3O_4, boil gently for 1–2 minutes, dilute and allow to settle. Violet colouration ($HMnO_4$). Alternatively, add 0·5 gram of sodium bismuthate to the HNO_3 solution, shake but do not heat, and allow to settle. Violet colouration ($HMnO_4$). **Mn present.**	**Filtrate.** May contain Na_2CrO_4 (yellow) and $NaAlO_2$ (colourless) dissolved in excess of NaOH solution. If colourless, Cr is absent and need not further be tested for. If yellow, Cr is indicated. Divide the liquid into 2 parts : (i) Add 1 gram of solid NH_4Cl, boil until only a faint odour of ammonia persists, and filter. White gelatinous ppt. of $Al(OH)_3$. **Al present.**§ The filtrate may be employed in tests for Cr. (ii) *Either* acidify with dilute H_2SO_4, cool thoroughly, add 2 c.c. of ether, and 1 c.c. of H_2O_2. Shake. Deep-blue colouration of ether layer (due to "perchromic acid") ; *or* acidify with acetic acid and add lead acetate solution ; yellow ppt. of $PbCrO_4$. **Cr present.**‡

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* The removal of interfering acid radicals (organic acids, borates, fluorides, silicates and phosphates) has been described in Tables XXIV and XXV ; see also Chapter VI.

§ Confirm Al by dissolving a portion of the ppt. in 5 c.c. of dilute HCl, add 5 c.c. of saturated ammonium acetate solution, and 5 c.c. of 0·1% "aluminon" solution (see under Aluminium, Sect. **III, 21**, reaction 7), shake, and then add NH_4OH solution until distinctly alkaline. A bright red flocculent ppt. ("lake") confirms Al.

A confirmatory test for Al, formerly widely employed, was the following. Dissolve the $Al(OH)_3$ ppt. in dilute HCl, add a few drops of $Co(NO_3)_2$ solution, soak up the solution and any ppt. in filter paper, wrap with a platinum wire and burn as in quantitative analysis. Heat the ash in a crucible strongly. A blue ash (Thenard's blue), confirms Al.

‡ *For footnote, see p.* 374

Explanation

The ppt. may contain $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$; some $MnO.(OH)_2$ (or MnO_2,H_2O) may also be present (see note 5 to Table XXVI; also under Manganese, Section **III, 26,** reaction *2*). The separation is based upon the following facts :—

(1) When the ppt. is boiled with NaOH solution and H_2O_2 (or with the equivalent Na_2O_2), the $Al(OH)_3$ is converted into soluble sodium aluminate $Na[AlO_2]$, and the $Cr(OH)_3$ is oxidised to the yellow, soluble sodium chromate Na_2CrO_4. The $Fe(OH)_3$ (and the $MnO.(OH)_2$, if present) remains undissolved. The excess of H_2O_2 is decomposed on boiling; any reduction of the chromate upon acidification is thus avoided.

$$Al(OH)_3 + NaOH = Na[AlO_2] + 2H_2O.$$

$$2Cr(OH)_3 + 3H_2O_2 + 4NaOH = 2Na_2CrO_4 + 8H_2O.$$

The $Fe(OH)_3$ is dissolved in dilute HCl and the resultant solution of $FeCl_3$ treated with KCNS solution or with $K_4[Fe(CN)_6]$ solution when a red colouration or blue precipitate is obtained.

$$FeCl_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KCl.$$

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

(2) Upon boiling the filtrate with NH_4Cl solution, the $Na[AlO_2]$ is decomposed, and Al is precipitated as $Al(OH)_3$.

$$Na[AlO_2] + NH_4Cl + H_2O = Al(OH)_3 + NaCl + NH_3.$$

(3) The tests for Cr in the yellow solution of Na_2CrO_4 involve : (*a*) the precipitation as insoluble $PbCrO_4$,

$$2Na_2CrO_4 + 2H.C_2H_3O_2 = Na_2Cr_2O_7 + 2Na.C_2H_3O_2 + H_2O,$$

$$Na_2Cr_2O_7 + 2Pb(C_2H_3O_2)_2 + H_2O$$
$$= 2PbCrO_4 + 2Na.C_2H_3O_2 + 2H.C_2H_3O_2;$$

or (*b*) the formation of the blue "perchromic acid," sometimes formulated as H_3CrO_8, unstable in cold aqueous solution, but more stable in cold ethereal solution,

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O,$$

$$Na_2Cr_2O_7 + H_2SO_4 + 7H_2O_2 = 2H_3CrO_8 + 5H_2O + Na_2SO_4.$$

‡ An alternative and more sensitive confirmatory test is the following. Add 1—2 c.c. of the diphenylcarbazide reagent to the solution acidified with dilute sulphuric or acetic acid. A deep red colouration is produced (see under Chromates, Section **IV, 33,** reaction *10*).

(4) The test for Mn consists in the conversion of the $MnO.(OH)_2$ into the nitrate by HNO_3, and into $HMnO_4$ by Pb_3O_4 (or PbO_2) or by $NaBiO_3$:

$$5PbO_2 + 2Mn(NO_3)_2 + 6HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O;$$

$$5Pb_3O_4 + 2Mn(NO_3)_2 + 26HNO_3 = 2HMnO_4 + 15Pb(NO_3)_2 + 12H_2O;$$

$$5NaBiO_3 + 2Mn(NO_3)_2 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O.$$

V,14. Table XXXIV.—Analysis of Group IIIB (Zinc Group)

The ppt. may contain NiS, CoS, MnS, ZnS and finely divided S. Wash thoroughly with 1% NH_4Cl solution containing a little ammonium sulphide solution; reject the washings. Transfer the ppt. to a small beaker or to a boiling tube. Add 20 c.c. of very dilute HCl (1 : 6), stir well, and allow to stand for 5 minutes. Filter.

Residue. May contain NiS and CoS. Test with borax bead. If blue, Co is indicated.

Dissolve the ppt. in a mixture of 2·5 c.c. of 10% NaOCl solution and 0·5 c.c. of dilute HCl. Add 1 c.c. of dilute HCl, and boil off excess of Cl_2. Cool, and dilute to 4–5 c.c. Divide the solution into 2 equal parts.

(i) Either—Add 2–3 grams of solid NH_4CNS, 2 c.c. of amyl alcohol, and shake thoroughly. Blue colour in the alcohol layer.

Or—Add a little dilute HCl and dilute acetic acid, followed by excess of freshly prepared α-nitroso-β-naphthol reagent and boil.

Red ppt.

Co present.

(ii) Add 2–3 c.c. of NH_4Cl solution, NH_4OH solution until alkaline, and then excess of dimethyl-glyoxime reagent; boil, if necessary. Red ppt.

Ni present.

Filtrate. May contain $MnCl_2$ and $ZnCl_2$, and possibly traces of $CoCl_2$ and $NiCl_2$. Boil off H_2S (test with lead acetate paper). Neutralise with NaOH solution, and add 5–10 c.c. in excess; then add 5 c.c. of Br_2 water. Boil for 2–3 minutes and filter.

Residue. Largely MnO_2 (+ traces of $Co(OH)_3$ and NiO_2 or $Ni(OH)_3$). Wash. Dissolve ppt. in 50% HNO_3 and a few drops of H_2O_2. Either boil with 1 gram of Pb_3O_4 (or PbO_2) or digest in the cold with 0·5 gram of $NaBiO_3$ (see Table XXXIII). Violet colouration ($HMnO_4$).

Mn present.

Filtrate. May contain $Na_2[ZnO_2]$. Add 2–3 c.c. of NH_4OH solution; boil to decompose excess of NaOBr. Divide solution into 2 parts.

(1) Pass H_2S or acidify with acetic acid and pass H_2S. White ppt. (ZnS).

(2) Acidify with acetic acid, and add $K_4[Fe(CN)_6]$ solution. White ppt. ($Zn_2[Fe(CN)_6]$).

Zn present*.

* Zn may be confirmed by Rinmann's green test. Dissolve the ppt. in a little dilute HNO_3, add 1–2 drops of $Co(NO_3)_2$ solution, soak up the solution in a piece of ashless filter paper, and ignite in a crucible (or burn first in a coil of Pt wire). The residue is coloured green.

Explanation

The separation of NiS, CoS, ZnS and MnS, which may be contained in the precipitate, is based upon the following facts :—

(1) MnS and ZnS dissolve readily in cold, very dilute HCl whilst NiS and CoS dissolve only very slightly.

$$MnS + 2HCl = MnCl_2 + H_2S\,;$$
$$ZnS + 2HCl = ZnCl_2 + H_2S.$$

The detection of Co and Ni in a mixture of CoS and NiS is carried out upon separate portions of the solution prepared by dissolving the sulphides in aqua regia. The tests are so delicate that moderate quantities of other elements do not appreciably interfere ; separation is therefore unnecessary.

$$3CoS + 2HNO_3 + 6HCl = 3CoCl_2 + 2NO + 3S + 4H_2O;$$
$$3NiS + 2HNO_3 + 6HCl = 3NiCl_2 + 2NO + 3S + 4H_2O.$$

The NH_4CNS test depends upon the formation of the blue ammonium cobaltothiocyanate $(NH_4)_2[Co(CNS)_4]$, which is soluble and comparatively stable in amyl alcohol. If Fe is present, red $Fe(CNS)_3$ is formed, which may obscure the blue colour ; the colour is then usually green. The addition of 0·5 c.c. of $SnCl_2$ solution and shaking, reduces the ferric salt to the colourless ferrous salt and the disturbing effect of the Fe is eliminated. It is essential to add solid NH_4CNS in order to secure the high concentration of NH_4CNS which is necessary for the success of this test.

The α-nitroso-β-naphthol $[C_{10}H_6(NO)OH]$ test yields a red precipitate of cobalti-nitroso-β-naphthol $[C_{10}H_6(NO)O]_3Co$, which is insoluble in cold dilute HCl or HNO_3. The corresponding Ni compound $[C_{10}H_6(NO)O]_2Ni$, is brown and soluble in HCl.

The dimethyl-glyoxime test for Ni gives a red precipitate of the Ni compound $(C_8H_{14}N_4O_4)Ni$. The reaction is not influenced by the presence of ten times as much Co as Ni. However, in the presence of Co, the latter combines preferentially forming a dark-coloured complex ion. An excess of the reagent must therefore always be added.

$$NiCl_2 + 2C_4H_8N_2O_2 + 2NH_4OH$$
$$= (C_4H_7N_2O_2)_2Ni + 2NH_4Cl + 2H_2O.$$

(2) When excess of NaOH solution is added to a solution containing $ZnCl_2$ and $MnCl_2$ (and, possibly, traces of $CoCl_2$

and $NiCl_2$), the hydroxides are first precipitated; the $Zn(OH)_2$, however, dissolves in excess of the reagent forming a solution of sodium zincate. It has been found best to add Br_2 water in order to oxidise the $Mn(OH)_2$ to MnO_2, because MnO_2 is less soluble than $Mn(OH)_2$ and a more complete separation of Mn and Zn is thus obtained.

$$MnCl_2 + Br_2 + 4NaOH = MnO_2 + 2NaBr + 2NaCl + 2H_2O;$$
$$ZnCl_2 + 4NaOH = Na_2[ZnO_2] + 2NaCl + 2H_2O;$$
$$2CoCl_2 + Br_2 + 6NaOH = 2Co(OH)_3 + 2NaBr + 4NaCl.$$

The test for Mn utilises the conversion of the MnO_2 by HNO_3 into $Mn(NO_3)_2$, and of the latter into $HMnO_4$ with Pb_3O_4 (see explanation of Table XXXIII).

$$MnO_2 + 2HNO_3 + H_2O = Mn(NO_3)_2 + O_2 + 2H_2O;$$
$$2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 = 2HMnO_4 + 15Pb(NO_3)_2 + 12H_2O.$$

(3) Before testing for Zn, the excess of NaOBr in the solution is eliminated by boiling with NH_4OH solution:

$$Br_2 + 2NaOH = NaBr + NaOBr + H_2O;$$
$$3NaOBr + 2NH_4OH = 3NaBr + N_2 + 5H_2O.$$

The precipitates of ZnS and $Zn_2[Fe(CN)_6]$ respectively are obtained in accordance with the equations:—

$$Na_2[ZnO_2] + H_2S = 2NaOH + ZnS;$$
$$Na_2[ZnO_2] + 4H.C_2H_3O_2 = Zn(C_2H_3O_2)_2 + 2Na.C_2H_3O_2 + 2H_2O;$$
$$2Zn(C_2H_3O_2)_2 + K_4[Fe(CN)_6] = Zn_2[Fe(CN)_6] + 4K.C_2H_3O_2.$$

Explanation (Table XXXV)

The addition of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ solutions precipitates $BaCO_3$, $SrCO_3$ and $CaCO_3$. $MgCO_3$ and $Mg(OH)_2$ are held in solution by the NH_4Cl. The large excess of NH_4^+ ions reduces the concentration of the CO_3^{--} ions, owing to the formation of HCO_3^- ions, to such an extent that the S.P. of $MgCO_3$ ($2{\cdot}6 \times 10^{-5}$) is not attained. $Mg(OH)_2$ is not precipitated as the high concentration of NH_4^+ ions lowers the OH^- ion concentration to such a value that the S.P. of $Mg(OH)_2$ ($3{\cdot}4 \times 10^{-11}$) is not exceeded (see under Magnesium, Section **III, 33,** reactions *3* and *1*).

All these carbonates dissolve in acetic acid forming solutions of the acetates:

$$BaCO_3 + 2H.C_2H_3O_2 = Ba(C_2H_3O_2)_2 + CO_2 + H_2O.$$

V, 15. Table XXXV.—Analysis of Group IV (Calcium Group)

Method A

The ppt. may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Wash with hot water and reject washings. Dissolve the ppt. in 10 c.c. of warm, dilute acetic acid * and boil for 1–2 minutes to expel CO_2. Test 2 c.c. of the solution for barium by heating to boiling and adding K_2CrO_4 drop-wise with shaking. A yellow ppt. ($BaCrO_4$) indicates Ba present.

Ba present.—Heat the remainder of the solution to boiling and add a slight excess of K_2CrO_4 solution (*i.e.*, until the solution assumes an orange tint), and filter the $BaCrO_4$. Treat the filtrate with NH_4OH solution until alkaline, followed by excess of $(NH_4)_2CO_3$ solution, and warm. A white ppt. indicates the presence of $SrCO_3$ and/or $CaCO_3$. Wash the ppt. with hot water and reject the washings; dissolve it in 5–10 c.c. of warm dilute acetic acid as above, and boil to remove excess of CO_2 (solution *A*).

Ba absent.—Throw away the portion used in testing for barium, and employ the remainder of the solution (*B*) to test for Sr and Ca.

Residue. Yellow: $BaCrO_4$. Wash well with hot water. Dissolve in a little concentrated HCl, evaporate almost to dryness, and apply the flame test.

Green flame.

Ba present.

Filtrate. Use acetic acid solutions *A* or *B*. Divide into 2 equal parts.

1. Render alkaline with NH_4OH solution, add 10–15 c.c. of boiling, saturated $(NH_4)_2SO_4$ solution, and place in a beaker of hot water for 5 minutes.

White ppt. ($SrSO_4$ and, possibly a little $CaSO_4$).

Sr present.

Confirm by transferring ppt. and filter paper to a crucible, heat until the paper has charred, add a few drops of concentrated HCl, and apply flame test. Crimson flame.

(*Note.* If Ca is present in considerable excess, the Ca flame will appear first, followed by the crimson Sr flame.)

2. To the cold solution add 3–4 g. NH_4Cl (the solution should be almost saturated) and excess of concentrated $K_4[Fe(CN)_6]$ solution Allow to stand for 5 minutes.

Pale yellow ppt.

Ca present.

One method of separation is based upon the following facts:—

(1) $BaCrO_4$ is insoluble in dilute acetic acid, whilst the chromates of Sr and Ca are soluble and are therefore not precipitated in dilute acetic acid solution ‡.

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* This operation is best carried out by pouring the hot acid over the ppt. in the filter paper, the extract being collected, warmed and repeatedly poured through the filter paper until all the residue has dissolved.

‡ The function of the acetic acid is to convert a portion of the CrO_4^{--} into $Cr_2O_7^{--}$, thus lowering the CrO_4^{--} ion concentration so that $SrCrO_4$ is not precipitated (see under Chromates and Dichromates, Section **IV, 33**). The solubility products are:

$BaCrO_4$ $2{\cdot}3 \times 10^{-10}$, $SrCrO_4$ $3{\cdot}5 \times 10^{-5}$, $CaCrO_4$ $2{\cdot}3 \times 10^{-2}$.

$$K_2CrO_4 + Ba(C_2H_3O_2)_2 = BaCrO_4 + 2K.C_2H_3O_2.$$

The treatment of $BaCrO_4$ with concentrated HCl converts it into the comparatively volatile $BaCl_2$, which is more suitable for the flame test.

(2) The precipitation of $SrSO_4$ with excess of concentrated $(NH_4)_2SO_4$ solution in faintly ammoniacal solution; the calcium forms the soluble $(NH_4)_2[Ca(SO_4)_2]$. If the calcium is present in very large excess, some $CaSO_4$ may be coprecipitated with the $SrSO_4$. However, if strontium is absent, no precipitate is obtained under the given experimental conditions.

Since $SrSO_4$ does not easily give a flame colouration, it is first partially reduced to SrS by the carbon from the filter paper; treatment of the residue containing SrS with HCl gives the relatively volatile $SrCl_2$.

(3) The formation of the relatively insoluble

$$Ca(NH_4)_2[Fe(CN)_6]$$

when a solution containing Sr and Ca acetates is treated with concentrated NH_4Cl solution and excess of $K_4[Fe(CN)_6]$ solution; the corresponding Sr compound is soluble.

An alternative method for separating Ca has been given in Table XXII. The Sr is precipitated as above with $(NH_4)_2SO_4$ solution as $SrSO_4$ and the latter filtered off; a sufficient concentration of Ca ions remain in the filtrate to give a precipitate of CaC_2O_4 with NH_4OH and $(NH_4)_2C_2O_4$ solutions.

Explanation (Table XXXVI)

This method utilises the following facts:—

(1) The carbonates of Ba, Sr and Ca are converted into the nitrates by treatment with HNO_3 and evaporation until dry.

$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + CO_2 + H_2O.$$

Of the three nitrates, only that of calcium is soluble in absolute ethyl alcohol; it can therefore be removed from the mixture by repeated extraction with this solvent.

(2) The separation of Ba and Sr is readily effected by precipitating the barium as $BaCrO_4$ as in *Method A*. After the removal of the barium, the strontium may be precipitated as $SrCO_3$ with NH_4OH and $(NH_4)_2CO_3$ solutions.

Table XXXVI.—Analysis of Group IV (Calcium Group)

Method B

The ppt. may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Dissolve it in dilute HNO_3 and evaporate *carefully* until the residue is quite dry. Do not heat strongly as this may decompose the nitrates.

Dissolve a part of the residue in a little water and add $CaSO_4$ solution. The following observations may be made :—(*a*) A ppt. is formed immediately ; Ba is present, and possibly Sr and Ca. (*b*) A ppt. forms slowly after standing for some time ; Sr, and possible Ca, is present ; Ba is absent. (*c*) No ppt. forms after standing ; Ca may be present.

Treat the dry residue with absolute ethyl alcohol (*inflammable*),* and filter through a filter paper which has been moistened with absolute alcohol.

Filtrate. Evaporate to dryness on the water bath.

White residue indicates Ca. Moisten residue with concentrated HCl and apply flame test. Brick-red flame.

Ca present.

Residue. May contain $Sr(NO_3)_2$ and $Ba(NO_3)_2$. If Ca present, repeatedly extract with absolute alcohol to remove all $Ca(NO_3)_2$ (*i.e.*, until a portion of the extract leaves no residue upon evaporation). Dissolve in water, add dilute acetic acid and excess of K_2CrO_4 solution. Boil and filter.

Residue. Yellow ; $BaCrO_4$.

Ba present.

Confirm by flame test, as in *Method A*.

Filtrate. Add NH_4OH solution and excess of $(NH_4)_2CO_3$ solution. White ppt. of $SrCO_3$.

Sr present.

Confirm by flame test, as in *Method A*.

An alternative method for separating Ba and Sr, which is not given in Table XXXVI, makes use of the fact that $SrCl_2$ is soluble in absolute ethyl alcohol whilst $BaCl_2$ is insoluble. The nitrates are converted into chlorides by repeated evaporation with concentrated HCl or by heating with solid NH_4Cl.

$$Sr(NO_3)_2 + 2NH_4Cl = SrCl_2 + 2NO + N_2 + 4H_2O.$$

Method B is more time-consuming than *Method A*, but has the advantage that each metal is almost completely separated.

Explanation (Table XXXVII)

The filtrate from Group IV may contain Mg^{++}, Na^+, K^+ and considerable quantities of ammonium salts. To test whether any of the metals are present, a portion of the solution is evaporated to dryness whereby all ammonium salts are volatilised ; a residue is indicative of the presence of one or all of these metals. There is no systematic scheme for separating these three metals satisfactorily in qualitative analysis; they are therefore tested for independently.

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* Dry acetone or butyl cellosolve, $C_4H_9O.CH_2.CH_2.OH$, b.p. 170·5°, are alternative solvents.

V,16. Table XXXVII.—Analysis of Group V (Alkali Group)

Add 1–2 c.c. of $(NH_4)_2SO_4$ solution and 1–2 c.c. of $(NH_4)_2C_2O_4$ solution to the main filtrate from Group IV, heat to boiling, cool, and allow to stand for 5 minutes. Filter, if necessary, and reject the ppt. This removes traces of Ca^{++}, Sr^{++} and Ba^{++} not precipitated in Group IV. Divide the solution into 2 unequal parts.

Smaller portion	*Larger portion*
Add NH_4OH solution, and then excess of Na_2HPO_4 solution. Cool, shake and rub the walls of the vessel with a glass rod. White crystalline ppt. of $Mg(NH_4)PO_4$. **Mg present.** To confirm Mg, or if the Na_2HPO_4 method gives doubtful results, employ the "magneson" reagent. Dissolve either the washed ppt. or preferably a little of the Group V residue in a little hot dilute HCl, add a few drops of the "magneson" reagent, followed by excess of 1% NaOH solution. A flocculent blue *ppt.* confirms Mg. (If only traces of Mg are present, a blue colouration is obtained. A blank test should, however, be carried out with the reagents.	Evaporate to dryness in a porcelain dish and heat the residue until no more fumes of ammonium salts are evolved (fume cupboard !). If no residue is obtained, Na and K are absent. If a solid remains, add 2–3 c.c. of water, and filter from any Mg compound, if present. Divide into 2 parts :— (i) Add a few drops of freshly prepared sodium cobaltinitrite solution* on a watch glass. Yellow ppt. **K present.** Confirm by flame test, using two thicknesses of cobalt glass; crimson flame. (ii) Add an equal volume of magnesium uranyl acetate reagent, shake and allow to stand. Yellow crystalline ppt. **Na present.** Confirm by flame test; persistent golden-yellow flame.

Examination for ammonium.—This has already been carried out with the original substance in the preliminary test (Section **V, 2,** test (v)).

Magnesium. The addition of NH_4Cl, NH_4OH and Na_2HPO_4 solutions to the cold solution results in the precipitation of white, crystalline $Mg(NH_4)PO_4$. This often separates slowly, due to supersaturation effects; precipitation is accelerated by vigorous shaking or by scratching the sides of the vessel with a glass rod.

$$MgCl_2 + NH_4OH + Na_2HPO_4 = Mg(NH_4)PO_4 + 2NaCl + H_2O.$$

* Dissolve 1 gram of the salt in 10 c.c. of water, and filter, if necessary. See, however, Section **A, 2.**

Owing to the slight solubility of the carbonates of the alkaline earth metals in ammonium salts, the filtrate from Group IV may contain small quantities of the metal ions (see Section **III, 33**), reaction *3*. Since these metal ions would also yield precipitates with Na_2HPO_4 solution and NH_4OH, they are first removed by the addition of solutions of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$.

$$BaCl_2 + (NH_4)_2SO_4 = BaSO_4 + 2NH_4Cl\,;$$
$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

The introduction of "magneson" (para-nitrobenzene-azo-resorcinol) (Section **III, 33,** reaction *8*), has made the identification of Mg in Group V a relatively simple matter since the alkali metals have no effect, although considerable quantities of ammonium salts may reduce the sensitivity of the reaction. The test depends upon the formation of a characteristically coloured "lake" of the precipitated $Mg(OH)_2$ with the reagent.

Potassium. Most of the precipitation reactions for K^+ ions are also given by NH_4^+ ions, hence the latter must first be removed by evaporation to dryness and ignition. Any MgO present in the residue is largely removed by making use of its slight solubility in water. The addition of sodium cobaltinitrite solution to a solution containing K^+ ions results in the precipitation of the bright yellow $K_2Na[Co(NO_2)_6]$ (see under Potassium, Section **III, 34,** reaction *1*).

$$Na_3[Co(NO_2)_6] + 2KCl = K_2Na[Co(NO_2)_6] + 2NaCl.$$

The flame test is a useful confirmatory test.

Sodium. Of the numerous reagents that have been proposed for sodium, one of the most satisfactory is magnesium uranyl acetate (see under Sodium, Section **III, 35,** reaction *1*). In the presence of a moderate concentration of Na^+ ions, a yellow (or greenish-yellow) precipitate of the compound $NaMg(UO_2)_3(C_2H_3O_2)_9,6{\cdot}5H_2O$ is obtained. Potassium and ammonium ions do not interfere.

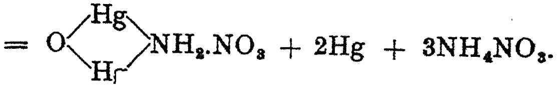
$$3UO_2(C_2H_3O_2)_2 + Mg(C_2H_3O_2)_2 + NaCl + H.C_2H_3O_2$$
$$= NaMg(UO_2)_3(C_2H_3O_2)_9 + HCl,$$

The production of a *persistent* golden yellow colour in the flame test is characteristic.

Ammonium was tested for in preliminary test (v) (Section **V, 2**) upon the original substance. It cannot be tested for in Group V since ammonium salts have been added in the course of the analysis. Heating of the original substance with NaOH solution liberates NH_3, which is identified by its odour and by its action upon red litmus paper. Owing to the danger of the NaOH solution spray affecting the litmus paper, the present author prefers to employ filter paper moistened with mercurous nitrate solution, which is blackened by ammonia.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O \text{ (heat) ;}$$

$$2Hg_2(NO_3)_2 + 4NH_3 + H_2O$$



$$= O\left\langle\begin{matrix}Hg\\Hg\end{matrix}\right\rangle NH_2.NO_3 + 2Hg + 3NH_4NO_3.$$

black

V, 17. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary dry tests with dilute sulphuric acid and with concentrated sulphuric acid (Section **V, 2,** tests (vi) and (vii)) will have provided useful information as to many acid radicals present. Furthermore, in the course of the examination for metal ions in solution, the presence *inter alia* of the following acid radicals will have been indicated :—

Chromate (or *dichromate*)—reddish-yellow solution becoming green and depositing white or yellowish-white sulphur ;

Permanganate—purple solution becoming nearly colourless and depositing sulphur ;

Arsenate—yellow precipitate of arsenious sulphide slowly formed in hot solution (see Note 2 to Table XXIV) ;

Silicate—insoluble residue of silica after evaporating filtrate from Group II to dryness ; and

Phosphate—tested for with nitric acid and ammonium molybdate solution before precipitating Group IIIA.

For the examination of acid radicals or anions, it is necessary to prepare a solution containing all (or most) of the anions free, as far as possible, from heavy metals. This is best prepared by boiling the substance with concentrated sodium carbonate solution ; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates * of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution. Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur

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* Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.

$$MA_2 + Na_2CO_3 \rightleftharpoons MCO_3 + 2NaA.$$

The carbonate MCO_3 is insoluble and the sodium salt NaA will pass into solution whether MA_2 is soluble in water or not.

Preparation of solution for testing for anions. Boil 2 grams of the finely-divided substance or mixture (1) with a saturated solution of pure sodium carbonate (2) (prepared from 4 grams of anhydrous sodium carbonate and 25 c.c. of distilled water) for 10 minutes, or until no further action appears to be taking place (3), in a small conical flask with a small funnel in the mouth to reduce the loss by evaporation; alternatively, a reflux condenser may be employed. Filter (4), wash the residue with hot distilled water and collect the washings together with the main filtrate; the total volume should be 30–40 c.c. Keep the residue (5). The sodium carbonate extract will be called the "*prepared solution.*"

Notes. (1) If a solution is supplied for analysis, use sufficient to contain 2 g. of solid material, render it strongly alkaline with saturated sodium carbonate solution and evaporate it down to 10–15 c.c.

(2) It is essential to use pure sodium carbonate; the A.R. product is satisfactory. Some "pure" samples may contain traces of sulphate or chloride: the absence of these impurities should be confirmed by a blank experiment.

(3) If ammonium is present, ammonia will be evolved (indicated by the smell above the solution), continue boiling until ammonia is completely expelled, otherwise those basic elements which form ammonia complexes may pass into the sodium carbonate extract.

(4) If no precipitate is obtained, the substance is free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required. Certain amphoteric elements may, however, be present in the sodium carbonate solution, *e.g.*, Cu, Sn, Sb, As, Al, Cr, and Mn, dissolve in appreciable quantities; manganates, permanganates, and chromates may also be present so that the colour of the solution should be noted. If cyanide is present, certain cations, such as Ag, Hg, Fe, Ni and Co, may pass into the alkaline extract by virtue of the formation of complex cyanides (anions).

(5) The residue from the Na_2CO_3 treatment may contain, in addition to the carbonates, basic carbonates and hydroxides of the heavy metals, certain phosphates (*e.g.*, those of Pb, Ag, Cd, Cr, Mo, Mn, Zn, Ca and Mg, which are less than 50 per cent. transposed), arsenates, sulphides, fluorides, silicates and complex cyanides, and the halides of silver. This may be due in the case of products produced by high-temperature processes or of certain natural products to the slow rate of reaction with the alkali carbonate or it may be due to the fact that the solubilities are such that very little metathesis can take place. Hence the residue should be kept until the tests for anions have been completed, and then tested for the above anions if they are not found in the alkaline extract or in the preliminary tests: the original substance can,

of course, be employed for these tests. After extraction of the sodium carbonate residue with dilute hydrochloric acid, the undissolved portion (R) may be treated as an insoluble substance and investigated according to Section **V, 21.** It is generally more convenient, however, to test the residue (R) for the various anions as follows.

Phosphate and arsenate. If the prepared solution, when acidified with dilute nitric acid, boiled for 1 minute, and rendered alkaline with ammonium hydroxide solution, does not give a precipitate with magnesia mixture, phosphate and arsenate are absent. Heat a small portion of the residue with concentrated nitric acid; if brown fumes are evolved, indicating the presence of a reducing agent, add more concentrated nitric acid and continue the heating until all the reducing agent is oxidised. Dilute the solution with water, heat to boiling and filter. Render the filtrate alkaline with concentrated ammonia solution, and add magnesia mixture. A white precipitate indicates *arsenate and/or phosphate*. Separate as described in Section **IV, 44,** *10* and *11*.

Sulphide. Reduce a portion of the residue with zinc and dilute sulphuric acid. If hydrogen sulphide is evolved (lead acetate paper test), *sulphide* is present. It is preferable to employ the sodium carbonate residue (R) rather than the original mixture in testing for sulphide, for the latter may contain sulphite and thiocyanate, both of which give hydrogen sulphide with nascent hydrogen (compare Sections **IV, 4,** *8*, and **IV, 10,** *5*).

Cyanide. If this is suspected, hydrogen cyanide will be evolved in the reduction with zinc and sulphuric acid, particularly on warming. Identify the hydrogen cyanide by the ammonium sulphide test (Section **IV, 8,** *1*).

Use the "prepared solution" to carry out the following tests.

1. Sulphate test. To 3 c.c. of the prepared solution add dilute hydrochloric acid until acid (test with litmus paper) and then add 2 c.c. in excess. Boil for 1–2 minutes to expel carbon dioxide completely, and then add about 1 c.c. of barium chloride solution. A white precipitate indicates *sulphate*. If time permits, confirm by test *1* in Section **IV, 24.**

Silicofluorides also give a white precipitate under the above conditions, but are of comparatively rare occurrence. They can be readily distinguished from sulphates by the action of concentrated sulphuric acid (Section **IV, 27,** *1*).

2. Test for reducing agents. Two procedures have been recommended; the first is more suitable for general use.

(a) Potassium permanganate test. Acidify 3 c.c. of the prepared solution with dilute sulphuric acid and add 1 c.c. of dilute sulphuric acid in excess. Add 3–4 c.c. of $0{\cdot}02N$ potassium permanganate solution (prepared by diluting 1 c.c. of $0{\cdot}1N$ $KMnO_4$ to 5 c.c.) from a dropper. Bleaching of the permanganate solution indicates the presence of one or more of the following reducing anions: *sulphite, thiosulphate, sulphide, nitrite, cyanide, thiocyanate, bromide, iodide, arsenite* and *ferrocyanide*. If the permanganate is not decolourised, heat and observe the result. If the reagent is bleached only on heating, the presence of *oxalate, formate or tartrate* is indicated. A negative test points to the absence of the above anions with the exception of cyanide, which, if present in low concentration, may not act upon the permanganate solution.

(b) $Fe[Fe(CN)_6]$ reagent test. This test is based on the following facts :—

(i) ferricyanides give only a brown colouration with ferric salts ;
(ii) substances with even moderate reducing action reduce ferricyanides to ferrocyanides, the latter reacting with ferric salts to give a dark blue precipitate of Prussian blue ;
(iii) with sulphites the ferric salt is preferentially reduced and a blue precipitate of Turnbull's blue is obtained.

To 4 c.c. of dilute HCl (1 : 4), add 3 drops of $FeCl_3$ solution, 2 drops of a *freshly prepared* saturated solution of A.R. $K_3[Fe(CN)_6]$ * followed by 2 c.c. of the prepared solution. Allow the mixture to stand for 2–3 minutes only. A blue precipitate or green colouration indicates the presence of *sulphide, sulphite, thiosulphate, nitrite, iodide, oxalate* (usually green colouration) *or ferrocyanide*. If a red colour is obtained (due to thiocyanate), filter the solution in order to render any blue precipitate visible.

3. Test for oxidising agents. Two procedures have been proposed ; the first is recommended for routine analysis.

(a) Manganous chloride reagent test. This test depends upon the fact that a saturated solution of manganous chloride ($MnCl_2,4H_2O$) in concentrated hydrochloric acid is converted by even mild oxidising agents to a dark brown-coloured manganic salt, probably containing the complex $[MnCl_6]^{--}$ or $[MnCl_4]^{--}$ ions.

To 2 c.c. of the prepared solution add 1 c.c. of concentrated hydrochloric acid and 2 c.c. of the manganous chloride reagent. A brown (or black) colouration indicates the presence of *nitrate, nitrite, ferricyanide, chlorate, bromate, iodate, chromate or permanganate*. A negative test indicates the absence of the above oxidising agents except small amounts of nitrates and nitrites and of arsenate ; if reducing anions have been found, this test is inconclusive.

(b) Iodide–CCl_4 test. The basis of this test of somewhat limited application is the oxidation of iodide in acid solution to iodine, which is readily identified with the aid of CCl_4.

Place 2 c.c. of the prepared solution in a test-tube (it is better to use a test-tube or small conical flask fitted with a ground glass stopper) and add 1–2 c.c. of CCl_4. Introduce 2 c.c. of dilute H_2SO_4 (to render the solution acid), followed by 2 c.c. of freshly-prepared 40 per cent. KI solution * added in 0·5 c.c. portions † (best with a dropper). Shake the mixture for 10–15 seconds. A purple to violet colour in the CCl_4 layer indicates the presence of *bromate, iodate, ferricyanide, persulphate, periodate, chromate or permanganate.* Chlorates and nitrates react very slowly.

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* Potassium ferricyanide solution is slowly reduced to the ferrocyanide on exposure to light, hence it is essential to prepare a fresh solution when required.

4. Tests with silver nitrate solution. The separation of a comparatively large number of anions from the prepared solution into several groups is possible with this reagent. The presence of ferrocyanide and/or ferricyanide, however, introduces difficulties in the subsequent separations, hence these must be tested for first and, if present, removed with cadmium nitrate solution in the presence of nitric acid.

Use is made of the following facts in separations with silver nitrate solution :—

(i) In dilute nitric acid solution (*ca.* 1·5*N* and *p*H about – 0·2) chloride, bromide, iodide, iodate and thiocyanate are precipitated.

(ii) Upon treatment of the filtrate from (i) with sodium nitrite solution and more silver nitrate solution, chlorate and bromate are reduced to the simple halides, the presence of which is revealed by the separation of silver chloride and silver bromide.

$$NaClO_3 + 3NaNO_2 = NaCl + 3NaNO_3.$$

Chromates (which, of course, yield a coloured solution) are simultaneously reduced to chromic salts.

(iii) If the acidity of the filtrate from (ii) is reduced (to about *p*H 5) by just neutralising with sodium hydroxide solution and adding dilute acetic acid, silver nitrate solution will precipitate phosphate, arsenate, arsenite,‡ oxalate and possibly other organic acids.

Acidify 10 c.c. of the prepared solution cautiously with dilute nitric acid (use litmus or other indicator paper). Determine the total volume of the acidified solution with the aid of a measuring cylinder, and add one-tenth of the volume of concentrated nitric acid. Boil in a porcelain dish to expel carbon dioxide and other volatile gases (1) for 2–5 minutes; filter, if necessary (2), and allow to cool. Use the solution (S) to carry out the tests given in the following table.

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* Iodide solutions are not stable because of oxidation by the atmosphere, hence they are best prepared immediately before use.

† Since iodine dissolves in KI solution to form the I_3^- ion, only a little of the KI solution is added at first so as to permit the small amounts of iodine to be more completely extracted by the CCl_4.

‡ Arsenite is unlikely to be found in the table of separation given below because of its oxidation to arsenate by the dilute nitric acid treatment of the prepared solution and also by other oxidising anions which may be present. Arsenite is, however, readily detected in the analysis for cations, compare Section **III, 11.**

<table>
<tr><td colspan="4">Add 1 c.c. of concentrated HNO_3 to the solution (S) (or to the filtrate from the ferro- or ferricyanide separation (3)), followed by $AgNO_3$ solution, slowly and with stirring, until precipitation is complete. (If no ppt. forms, do not add more than 0·5 c.c. of $AgNO_3$ solution.) Filter and wash with very dilute HNO_3 (1 : 20).</td></tr>
<tr><td rowspan="3">Residue (<i>A</i>)
Yellow or white.
AgCl
AgBr
AgI
$AgIO_3$ (4)
AgCNS
Use <i>Table A</i></td><td colspan="3">Filtrate. Add 1 c.c. of $AgNO_3$ solution, then 20% $NaNO_2$ solution (5) (6) until precipitation is complete. (If no ppt. forms, do not add more than 0·5 c.c. of $NaNO_2$ solution.). Filter and wash with very dilute HNO_3 (1 : 20).</td></tr>
<tr><td rowspan="2">Residue (<i>B</i>)
White or pale yellow.
<i>Bromate and/or Chlorate</i> (7) <i>present.</i></td><td colspan="2">Filtrate. Add NaOH solution dropwise (use a dropper) until neutral to litmus (8), then 0·5 c.c. of dilute acetic acid, followed by 1 c.c. of $AgNO_3$ solution, and heat the mixture to about 80° (9). If a permanent ppt. forms, add more $AgNO_3$ solution until precipitation is complete. Filter and wash with hot water.</td></tr>
<tr><td>Residue (<i>C</i>) (10).
Ag_3PO_4 yellow.
Ag_3AsO_4 reddish-brown.
$Ag_2C_2O_4$ white (11)
Use <i>Table C.</i></td><td>Filtrate.
Reject.</td></tr>
</table>

Notes. (1) This will expel all the CO_2 and most of the other volatile gases—SO_2 from sulphites, SO_2 and finely divided S from thiosulphates; H_2S from sulphides; HCN from cyanides, ferro- and ferricyanides; CO_2 and a little HCNO (odour reminiscent of SO_2) from cyanates; NO_2 from nitrites; O_2 from H_2O_2 derived from peroxides and persulphates.

If H_2S or SO_2 is evolved, partial oxidation to sulphuric acid will occur. Arsenite, if present, will also be largely oxidised to arsenate, hence no provision for the identification of arsenite is made in the table. Iodide will be partially oxidised by the nitric acid to iodine, which will be readily identified by the brown colour of the solution; the presence of iodide will also have been indicated in the preliminary test with concentrated sulphuric acid. Bromides are only slightly oxidised to bromine by the nitric acid of the concentration employed (*ca.* 1·5*N*).

If ferro- or ferricyanide is present, it is partially decomposed with the evolution of HCN and the production of a dark brown to black solution.

(2) A precipitate here suggests the presence of arsenic, antimony or tin sulphides, originating from the corresponding thio-salts. Other precipitates which may also appear here are silicic acid from silicates, lead, stannous, aluminium and zinc hydroxides from salts of these amphoteric metals, and cyanides from less stable complex cyanides, *e.g.*, $[Ag(CN)_2]^-$, $[Cu(CN)_4]^{---}$ and $[Cd(CN)_4]^{--}$.

(3) Because of the interfering effect of ferro- and ferricyanides upon subsequent tests, these must be removed first, if present. These anions may have been partially decomposed by the HNO_3 treatment (see Note (1) above). Test as follows.

Ferrocyanide (and Thiocyanate). Acidify 1 c.c. of the prepared solution with dilute HCl and add a few drops of $FeCl_3$ solution. A deep blue precipitate indicates *ferrocyanide present.* Add 0·5–1 c.c. of $FeCl_3$ solution and 0·2 g. of NaCl (to facilitate the subsequent filtration). Shake the mixture, add a little " Gooch " asbestos or filter paper pulp, and filter. A deep red filtrate indicates *thiocyanate present.*

Ferricyanide. Acidify 1 c.c. of the prepared solution with dilute HCl, and add a few drops of freshly prepared $FeSO_4$ solution. A deep blue precipitate indicates *ferricyanide present.* This should not be confused with the light grey-blue precipitate usually produced by ferrocyanide.

If ferro- or ferricyanide is present, remove it completely by strongly acidifying with nitric acid (10 c.c. of the prepared solution and 6 c.c. of 1 : 2 HNO_3), adding 10% $Cd(NO_3)_2$ solution dropwise and with vigorous shaking until precipitation is complete. Filter after standing for 5 minutes ; shake the mixture from time to time. If the filtration is difficult, mix a little " Gooch " asbestos with the precipitate. Wash with a solution containing 1 c.c. of 10% $Cd(NO_3)_2$ solution and 20 c.c. of dilute HNO_3 (1 : 20). Employ the filtrate for the $AgNO_3$ solution tests.

(4) As the subsequent separation (*Table A*) does not distinguish between iodide and iodate, it will be necessary if the latter is suspected (oxidising agents test positive), to test for iodate by acidifying with dilute HCl, reducing with defect of SO_2 or a little $NaHSO_3$ in the presence of 1–2 c.c. of CCl_4 ; a blue colouration of the latter indicates *iodate present* (compare Section **IV, 21,** test *5*).

(5) The $NaNO_2$ must be halogen-free. The A.R. reagent is suitable ; any other product must be tested for chloride with $AgNO_3$ solution.

(6) If the solution is yellow, chromate is indicated. This will be reduced to the chromic state by the $NaNO_2$ solution.

(7) Separate chloride and bromide as detailed in *Table A*. If chloride is absent in residue *A* and found in residue *B*, then chlorate is present. If, however, chloride is found in residue *A*, then chlorate and/or hypochlorite may be present, since hypochlorites are converted to chlorates by the sodium carbonate treatment.

To **detect hypochlorite and chlorate in a mixture,** extract about 0·5 gram of the powdered original mixture with 15–20 c.c. of cold water and filter. Divide the extract into two equal parts.

(*a*) Acidify one half slowly with dilute acetic acid (1 : 2), add 2 c.c. of lead acetate solution, heat to boiling and allow to stand. A brown precipitate (PbO_2) indicates the presence of *hypochlorite*.

(*b*) To test for chlorate, the hypochlorite must first be removed. Dilute the other half of the solution with twice its volume of water, add 5 c.c. of dilute nitric acid, 5 c.c. of 10% sodium arsenite solution and

5 c.c. of silver nitrate solution (the sodium arsenite reduces the hypochlorite, but not the chlorate, to chloride). Filter off the precipitated silver chloride, treat the filtrate with a little more silver nitrate solution and 1 c.c. of 5% sodium nitrite solution (chloride-free). A white precipitate indicates the presence of *chlorate*.

(8) The sodium hydroxide solution should be added until the first permanent precipitate of *C* or of brown silver oxide appears. The solution must not be allowed to become alkaline to litmus for this will produce a large precipitate of silver oxide which redissolves only slowly.

The *p*H required for the precipitation of *C* is about 5·5; this can be more conveniently achieved by the use of either nitrazine (sodium dinitrophenyl-azo-naphthol sulphonate) or bromocresol purple (dibromo-*o*-cresol-sulphone-phthalein) test-papers. All that is necessary is to add the sodium hydroxide solution until the appropriate colour change is produced; it is best to use a standard for comparison (nitrazine, *p*H range 5·5–7·2, yellow to blue; bromocresol purple, *p*H range 5·2–6·8, yellow to purple).

(9) A crystalline precipitate of silver acetate may separate here; this dissolves when the solution is heated.

(10) Chromate, if present, would normally be precipitated at a *p*H of about 5·5, but the sodium nitrite treatment in *B* reduces it to the chromic state. Chromic hydroxide is not precipitated in the acetic acid–acetate solution unless present in very large amounts.

(11) Other organic acids may also separate here. If only a white precipitate is obtained, use the organic acids separation table of Section **IV, 44,** *19*. The presence of organic acids will also be indicated by some of the preliminary tests.

Table A

Thiocyanate test. Test one-quarter of the ppt. *A* for thiocyanate by heating for 3–4 minutes with 5% NaCl solution (this converts part of the AgCNS into NaCNS), cool, and allow the ppt. to settle. Treat the supernatant liquid with 1 c.c. of dilute HCl and a few drops of $FeCl_3$ solution. Red colouration. *Thiocyanate present.*

If thiocyanate is present, it must be destroyed since it interferes with the tests for the halides. Heat the remainder of the ppt. *A* in a porcelain crucible, gently at first and then gradually to dull redness until all the thiocyanate is decomposed, *i.e.*, until blackening of the ppt. and/or burning of S ceases.

To the residue in the crucible (if thiocyanate is present) or to the remainder of the ppt. *A* transferred to a small beaker (if thiocyanate is absent), add 1–2 g. of granulated zinc (but preferably 20 mesh) and 5–10 c.c. of dilute H_2SO_4. Allow the reduction to proceed for 10 minutes with frequent stirring. Filter and wash the ppt. with a little dilute H_2SO_4. Divide the filtrate into three equal parts.*

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* The preliminary test with concentrated H_2SO_4 will generally indicate the presence of any of the three halides or mixtures of them. For individual halides, the confirmatory tests of Section **V, 18,** may be used. If mixtures are present, the methods described in Section **IV, 44,** *5–7*, may be adopted. For those who prefer systematic testing for any or all of the halides, the alternative procedures in *Table A* are recommended.

Iodide test (compare Note (1) above). Add 1 c.c. of CCl_4 and 3 c.c. of 10-volume H_2O_2 *or* 3 c.c. of 25% $Fe_2(SO_4)_3$ solution to one-third of the filtrate. Shake vigorously and allow to settle. Purple to violet colouration of CCl_4 layer. *Iodide* (*or iodate*—see Note (4) above) *present.*

Bromide test. (*a*) If iodide is present, this must be removed by treating one-third of the solution with 5 c.c. of dilute H_2SO_4 and 2 c.c. of 30% $NaNO_2$ solution (chloride-free). Boil the solution with stirring, concentrate to 3 c.c., and allow to cool. Test for bromide as under (*b*).

(*b*) If iodide is absent, use one-third of the solution directly. Add an equal volume of concentrated HNO_3, immerse the test-tube in a beaker of boiling water for 2 minutes, and cool to room temperature with cold water. Add 1–2 c.c. of CCl_4 and stir vigorously with a glass rod (if a glass-stoppered tube or conical flask is available, this will facilitate shaking). Yellow or brown colour of the CCl_4 layer. *Bromide present.*

Chloride test. (*a*) If iodide and/or bromide present, dilute the remaining third of the solution to 15 c.c., add 8 c.c. of concentrated HNO_3 and boil (glass rod in beaker) for 5 minutes or until no more Br_2 is given off. Cool and test for chloride as in (*b*) below with $AgNO_3$ solution only.

(*b*) If bromide and iodide are absent, add 3–4 c.c. of dilute NHO_3 and 3 c.c. of $AgNO_3$ solution; stir and heat to boiling. White ppt. *Chloride present.*

Alternative Procedure for Chloride in the Presence of Bromide with Iodide Absent. (Acetone-Permanganate Method.*) To 3 c.c. of the solution in a small conical flask, add 3 c.c. of concentrated H_2SO_4 slowly and with great care. Cool to room temperature (use running tap water), and add 3 c.c. of acetone (free from reducing agents, *e.g.*, A.R.) and cool again. Treat the solution with $0{\cdot}1$–$0{\cdot}2N$ $KMnO_4$, 2–3 drops at a time, with swirling, until a faint colour of the permanganate just appears. Reduce the excess of permanganate with a few drops of H_2O_2 solution, and add $AgNO_3$ solution. White ppt. *Chloride present.*

Theory. The acetone and permanganate convert the bromine into bromoacetone, which does not give a precipitate with $AgNO_3$ solution.

$$\begin{aligned}&10CH_3COCH_3 + 5Br_2 + \\ &\qquad 2KMnO_4 + 3H_2SO_4 = 10CH_3COCH_2Br + \\ &\qquad\qquad K_2SO_4 + 2MnSO_4 + 8H_2O.\end{aligned}$$

As soon as all the halogen is converted into bromacetone, the excess of permanganate is readily identified by the colour. It is essential to keep the solution cool in running water and also 10–12N with sulphuric acid. If the acid concentration is much higher or if the solution is allowed to become warm, appreciable loss of chlorine may occur when excess of permanganate is added. Hence as soon as the end-point is reached, the solution should be swirled to rinse down any drops of permanganate solution on the side of the flask and the excess of permanganate immediately reduced with a few drops of hydrogen peroxide to prevent loss of chlorine.

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* Compare the highly satisfactory method given in Section **IV, 44,** *5, Method B.*

Table C

If the ppt. is white, only organic acids may be present and the other anions need not be tested for. Furthermore, the preliminary tests of heating alone and with concentrated H_2SO_4 will have given an indication of the presence of organic acids. If organic acids are indicated or suspected, use the organic acids separation table of Section **IV, 44,** *19*.

If the precipitate is yellow, phosphate is present and arsenate is absent. Confirm phosphate by pouring 15 c.c. of dilute HCl repeatedly through the filter paper: return the residue (mainly AgCl) to the silver residues bottle. Render the extract alkaline with dilute NH_4OH solution (1 : 1) and add 5 c.c. in excess.* Add about 10 c.c. of magnesia mixture to the solution and allow to stand. A white ppt. confirms ***phosphate.***

If the ppt. is reddish-brown, the ppt. obtained with magnesia mixture as detailed in the preceding paragraph may consist of a mixture of $MgNH_4PO_4$ and $MgNH_4AsO_4$. Separate and identify by procedure *10* of Section **IV, 44.**

5. Test with calcium chloride solution. For tests **5–7** a "*neutral solution*" is required. This is prepared as follows. Take 10 c.c. of the prepared solution in a porcelain dish and render it faintly acid with dilute nitric acid (use litmus paper or other equivalent test-paper). Boil for 1–2 minutes to expel carbon dioxide, allow to cool, then add dilute ammonium hydroxide solution until just alkaline † and boil to expel the excess of ammonia. Divide the solution into three equal parts for tests **5, 6** and **7**.

Add $CaCl_2$ solution (equal in volume to that of the solution) and allow to stand for several minutes. A white precipitate indicates *fluoride, oxalate, phosphate, arsenate and tartrate*; ‡

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* If chromate was present in the original material, it will have been reduced to a chromic salt by the $NaNO_2$ treatment and may be partially precipitated in *C*, particularly if the concentration was high. It will be dissolved by the HCl and then be reprecipitated by the NH_4OH solution. Hence any precipitate formed here must be filtered off before the magnesia mixture is added.

† If a precipitate forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric elements (lead, tin, aluminium and zinc) is indicated. The precipitate should be filtered off and rejected.

‡ $CaSO_4$ and $Ca(BO_2)_2$ may separate from sufficiently concentrated solutions.

a precipitate which separates on boiling for 1–2 minutes is *citrate*. Of these only oxalate and fluoride are insoluble in dilute acetic acid. Hence extract the white precipitate with dilute acetic acid and filter. A residue (*R*) insoluble in dilute acetic acid, indicates *oxalate and/or fluoride*. Exactly neutralise the acetic acid solution by adding sodium hydroxide solution from a dropper and testing with an indicator paper or solution (bromothymol blue or nitrazine yellow is suitable) ; a white precipitate indicates the presence of phosphate, arsenate and/or tartrate.

It is convenient to test the residue *R* for oxalate here. Dissolve it by pouring hot dilute sulphuric acid into the filter. Treat the hot filtrate with a few drops of potassium permanganate solution. If the permanganate solution is reduced, *oxalate is present*. If no reduction occurs, the presence of fluoride is indicated.

6. Test with ferric chloride solution. Treat the second third of the " neutral solution " drop by drop with ferric chloride solution until no further change occurs.

(The bench reagent contains free hydrochloric acid ; add sodium carbonate solution until a precipitate just forms, filter and use the filtrate for the test.)

Yellow to brown precipitate.	*Benzoate, succinate* (also *chromate, phosphate, arsenate* and *borate*, all of which have been or will be found by other tests).
Blue precipitate.	*Ferrocyanide.*
Reddish-brown colouration, ppt. after dilution and boiling.	*Acetate, formate.*
Blood-red colouration, discharged by $HgCl_2$ solution.	*Thiocyanate* (*sulphocyanide*).
Reddish-purple colouration; colour vanishes on warming.	*Thiosulphate.* †
Brown colouration; blue ppt. with $FeSO_4$ solution.	*Ferricyanide.*
Violet colouration.	*Salicylate.*
Greenish-black colouration.	*Gallate.*
Bluish-black colouration.	*Tannate.*

7. Test for silicate. To the remaining third of the " neutral solution " add ammonium chloride and ammonium carbonate solution. A gelatinous precipitate indicates *silicate*.

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† As a general rule, thiosulphate will not be found here as it should have been more or less completely decomposed in the preparation of the " neutral " solution.

A more satisfactory reagent for the precipitation of silicates is hexammine zinc hydroxide, $[Zn(NH_3)_6](OH)_2$. This precipitates zinc silicate $ZnSiO_3$, which is much more difficultly soluble in dilute alkaline solution than is the free silicic acid.

$$Na_2SiO_3 + [Zn(NH_3)_6](OH)_2 = ZnSiO_3 + 2NaOH + 6NH_3.$$

The reagent is added in slight excess and the solution boiled until all the ammonia is expelled.

The *reagent* is prepared by treating pure zinc nitrate solution with potassium hydroxide solution, filtering off the precipitated zinc hydroxide, washing well, and dissolving the precipitate in dilute ammonium hydroxide solution.

8. Test for fluoride. The presence of fluoride will have been indicated in the preliminary test with concentrated sulphuric acid by the " oily " or " greasy " appearance of the tube and also by the calcium chloride solution test. It may be confirmed by the following test.

Fit a small test-tube with a cork carrying a piece of glass tubing open at both ends ; cut a V-shaped groove in the side of the cork to allow for the expansion of the air in the tube when heated. Mix a small quantity of the original substance in a crucible with about three times its bulk of ignited silica (quartz powder is preferable, but results are obtained with precipitated silica), transfer it carefully to the tube, and add by means of a dropper or small pipette about twice the volume of concentrated sulphuric acid as there is solid. Introduce the glass tube, wet on the inside with water thus forming a ring of water at the lower end (Fig. 48), into the test-tube and adjust its height so that the bottom is at a distance of approximately one and a half times the diameter of the tube from the paste in the test-tube. Heat the mixture *gently* over a small flame for 2–3 minutes. A white film of silicic acid in the water confirms the presence of *fluoride*.

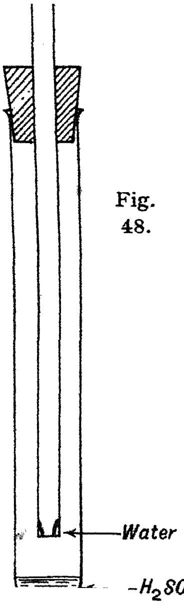

Fig. 48.

The reactions which occur are :

$$MF_2 + H_2SO_4 = MSO_4 + 2HF ;$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O ;$$
$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2[SiF_6].$$

When the highly reactive precipitated silica is employed, much of the SiF_4 reacts with it to form a stable oxyfluoride, probably

$$SiF_4 + SiO_2 = 2SiOF_2.$$

Hence the relatively unreactive powdered quartz is to be preferred.

9. Test for cyanide. This is sometimes missed in the preliminary test with dilute sulphuric acid and in the potassium permanganate test for reducing anions. The following test is conclusive. Use the apparatus described in the test for ammonia (Fig. 43) with Nessler's reagent. Place 0·2–0·3 gram of the substance in the test-tube or distilling flask, place the long delivery tube with the end dipping into 5 c.c. of 20 per cent. sodium hydroxide solution in the test-tube. Warm gently until about one-third of the liquid has distilled over. Add a few drops of freshly prepared, saturated ferrous sulphate solution, heat to 80–90° and cool to room temperature. Carefully acidify with concentrated hydrochloric acid and add a few drops of ferric chloride solution. A blue precipitate of Prussian blue confirms *cyanide*. With small amounts of cyanide, a blue or blue-green colouration is obtained.

10. Test for chromate. If the prepared solution is colourless, chromate is absent. If yellow, chromate may be present ; ferro- and ferri-cyanides also impart a yellow colour to the solution. The presence of chromate will have been indicated by the precipitation of green chromic hydroxide in the silver nitrate solution tests (*Table C*) and also in the analysis for cations.

To confirm chromate, acidify 2 c.c. of the prepared solution with dilute sulphuric acid, add 1–2 c.c. of amyl alcohol, followed by 1–2 c.c. 10-volume hydrogen peroxide and shake gently (compare Section **IV, 33,** *4*). A blue colouration of the amyl alcohol layer confirms *chromate.*

11. Test for periodate (1). This anion will give a positive test for oxidising agents, but will not be detected in the systematic analysis. It will be necessary to first remove iodide or iodate by precipitation with silver nitrate in acid solution, and the excess of silver ions with sodium chloride solution : the resultant solution is strongly acidified with hydrochloric acid and a ferrous salt is added. If a periodate is present, it will be reduced to iodine, which can be identified with carbon tetrachloride.

Acidify 3 c.c. of the prepared solution with 60 per cent. perchloric acid and add 1 c.c. in excess (2) ; add silver nitrate solution, slowly and with stirring, until precipitation is complete. Filter and collect the filtrate in a ground-glass stoppered conical flask or test-tube. Add 5 per cent. sodium chloride solution, 0·5 c.c. at a time, to the filtrate until no more precipitate forms. Stopper the flask or test-tube and shake the mixture vigorously after each addition. Filter off the silver chloride (3), transfer the filtrate to the stoppered vessel, add an equal volume of concentrated hydrochloric acid (if a precipitate of sodium chloride forms, filter), cool, then add 1–2 grams of solid ferrous ammonium sulphate and 2 c.c. of carbon tetrachloride. Shake the mixture intermittently for 5 minutes. A purple colour in the carbon tetrachloride indicates *periodate present.*

Notes. (1) This anion is rarely encountered and need not be tested for in general qualitative analysis. It is given here for the sake of completeness as no reactions for periodates are included in Chapter IV. Two tests which **distinguish periodates from iodates** are :

(*a*) with mercuric nitrate solution an orange-red precipitate of $I_2O_7,5HgO$ is obtained (compare iodates which give white $Hg(IO_3)_2$) ;

(*b*) on boiling with 10 per cent. nitric acid and a little manganous sulphate solution, a purple solution of permanganic acid is produced (compare iodates, which do not yield permanganic acid).

(2) Nitric acid tends to oxidise ferrous iron, hence it is advisable to maintain the nitrate ion concentration as low as possible and to keep the solution cold.

(3) The excess of silver ions is removed as silver chloride because they are reduced by ferrous salts to silver.

The preliminary dry tests and the reactions in solution described above will give a general (and, in some cases, a particular) indication of the nature of the acid radicals or anions present. For a number of anions (*e.g.*, thiocyanate, chloride, bromide, iodide, iodate, bromate, chlorate, phosphate, silicate, fluoride, cyanide and chromate), the tests are more or less conclusive. However, in the presence of mixtures of anions, it will be necessary to distinguish between those which give analogous reactions, for example, (i) sulphite, thiosulphate and sulphate ; (ii) chloride, chlorate and perchlorate ; (iii) arsenite, arsenate and phosphate ; (iv) ferricyanide and ferrocyanide ; (v) acetate and formate ; (vi) succinate and benzoate ; and (vii) oxalate, tartrate and citrate. In some cases one anion interferes with the reaction of the other, *e.g.*, (viii) carbonate and sulphite ; (ix) nitrite and nitrate ; (x) nitrate in the presence of bromide, iodide, chlorate and perchlorate ; (xi) iodate and iodide ; (xii) oxalate and fluoride ; and (xiii) chloride and cyanide. This subject is fully discussed in Section **IV, 44.** Particular attention is directed to the table of separation of organic acids (Section **IV, 44,** *19*) : this must be used with due consideration as to the influence of interfering organic acids (compare tests **5** and **6**).

V, 18. CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

In every case where the presence of any acid has been indicated, it must be confirmed by at least one distinctive confirmatory test. Conclusive tests for anions (halides, sulphate, oxy-halides, thiocyanate, phosphate, silicate, fluoride, cyanide and chromate) have already been given in Section **V, 17**; it will, of course, be unnecessary to confirm these further. The following list, which, for the sake of completeness includes those anions already referred to, will assist the student in the choice of these. Full experimental details will be found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (**IV, 2,** *7*) is to be interpreted as Section **IV, 2,** reaction *7*. It is assumed, of course, that interfering acids are absent or have been removed.

Chloride. (i) Heat solid with concentrated H_2SO_4 and MnO_2; Cl_2 evolved (bleaches litmus paper and also turns KI-starch paper blue) (**IV, 14,** *2*). (ii) Chromyl chloride test (**IV, 14,** *5*). (iii) Silver chloride-sodium arsenite test (**IV, 14,** *3*).

Bromide. (i) Heat solid with concentrated H_2SO_4 and MnO_2; Br_2 evolved (**IV, 15,** *2*). (ii) Chlorine water and $CHCl_3$ or CCl_4 test; yellowish-brown to yellow colouration (**IV, 15,** *5*).

Iodide. (i) Chlorine water and $CHCl_3$ or CCl_4 test; violet colouration (**IV, 16,** 4). (ii) Chlorine water and starch paste test; blue colouration (**IV 16,** *4*).

Fluoride. (i) Etching test (**IV, 17,** *2*). (ii) Silicon tetrafluoride test (heat with concentrated sulphuric acid in a test-tube((**IV, 17,** *1*); better, test **8** in **V, 17**. (iii) Zirconium-alizarin test (**IV, 17,** *6*).

Cyanide. (i) Prussian blue test (**IV, 8,** *4*); better, test **9** in **V, 17**. (ii) Ammonium sulphide test (**IV, 8,** *1*, *5*).

Nitrite. (i) Brown ring test with dilute acetic acid or with dilute sulphuric acid (**IV, 7,** *2*). (ii) Thiourea test (**IV, 7,** *9*). (iii) Sulphanilic acid-α-naphthylamine reagent test (**IV, 7,** *10*).

Nitrate. (i) Brown ring test with concentrated H_2SO_4 (**IV, 18,** *3*). (ii) Ammonia test with Devarda's alloy (**IV, 18,** *4*).

Sulphide. (i) Dilute H_2SO_4 on solid, and action of H_2S on lead acetate paper (**IV, 6,** *1*). (ii) Sodium nitroprusside test (**IV, 6,** *6*).

Sulphite. (i) Dilute H_2SO_4 on solid, and action of SO_2 upon potassium dichromate paper (**IV, 4,** *1*). (ii) Nascent hydrogen test (**IV, 4,** *8*).

Thiosulphate. (i) Action of dilute H_2SO_4 upon solid, and liberation of SO_2 (dichromate paper test) and sulphur (**IV, 5,** *1*). (ii) Potassium cyanide test (**IV, 5,** *6*). (iii) Nickel ethylenediamine test (**IV, 5,** *9*).

Sulphate. (i) $BaCl_2$ solution and dilute HCl test, and reduction to sulphide (test for latter with sodium nitroprusside or lead acetate solution) (**IV, 24,** *1*).

Carbonate. (i) Action of dilute H_2SO_4 upon solid, and lime water test (**IV, 2,** *1*).

Hypochlorite. (i) Action of dilute HCl, and test for Cl_2 evolved (**IV, 13,** *1*). (ii) Cobalt nitrate solution test (**IV, 13,** *4*).

Chlorate. (i) Indigo test (**IV, 19,** *7*). (ii) Ferrous sulphate test (**IV, 19,** *6*). (iii) Action of heat (**IV, 19,** *10*). (iv) Sodium nitrite test (**IV, 19,** *4*; also test **4** in **V, 17**).

Bromate. (i) Action of concentrated H_2SO_4; Br_2 and O_2 evolved (**IV, 20,** *1*). (ii) Hydrobromic acid test (**IV, 20,** *4*).

Iodate. (i) Potassium iodide test (**IV, 21,** *6*). (ii) Sulphur dioxide or hydrogen sulphide test (**IV, 21,** *5*).

Perchlorate. (i) Action of heat and test for chloride (**IV, 22,** *7*), and indigo test (**IV, 22,** *4*).

Borate. (i) Flame test (**IV, 23,** *2*; better, test (**IX**) in **V, 3**). (ii) Turmeric paper test (**IV, 23,** *2*).

Silicate. (i) Microcosmic bead test (**IV, 26,** *6*) and silicon tetrachloride test (**IV, 26,** *6*). (ii) Ammonium molybdate solution and $SnCl_2$ solution test (**IV, 26,** *5*).

Silicofluoride. (i) Action of concentrated H_2SO_4 and $BaCl_2$ solution test (**IV, 27,** *1, 2*).

Persulphate. (i) Action of boiling water (**IV, 25,** *1*). (ii) Manganous sulphate solution test (**IV, 25,** *5*).

Chromate. (i) Hydrogen peroxide test (**IV, 33,** *4*). (ii) Lead acetate solution test (**IV, 33,** *3*). (iii) Action of hydrogen sulphide or sulphur dioxide (**IV, 33,** *5, 6*). (iv) Solid when warmed with a solid chloride and concentrated H_2SO_4 evolved chromyl chloride (**IV, 14,** *5*). (v) Diphenylcarbazide reagent test (**IV, 33,** *10*).

Permanganate. (i) Hydrogen peroxide test, and identification of Mn^{++} ion (**IV, 34,** *1*). (ii) Action of oxalic acid, and identification of Mn^{++} ion (**IV, 37,** *4*). (iii) Action of hydrogen sulphide or sulphur dioxide (**IV, 34,** *2*).

Arsenite. (i) Action of H_2S upon acid solution (**III, 11,** *1*). (ii) Copper sulphate solution test (**III, 11,** *4*), silver nitrate solution test (**III, 11,** *2*), and absence of precipitate with magnesia mixture (**III, 11,** *3*) or on boiling with ammonium molybdate solution and nitric acid. (iii) Bettendorff's test (**III, 11,** *6*).

Arsenate. (i) Action of H_2S on acid solution (**III, 12,** *1*), and silver nitrate solution test upon neutral solution (**III, 12,** *2*). (ii) Magnesia mixture test (**III, 12,** *3*). (iii) Ammonium molybdate test (**III, 12,** *4*).

Orthophosphate. (i) Ammonium molybdate test (temperature not above 40°) (**IV, 28,** *4*). (ii) Magnesia mixture test (**IV, 28,** *3*).

Phosphite. (i) Silver nitrate solution test (**IV, 30,** *1*), and Zn + dilute H_2SO_4 test (**IV, 30,** *6*).

Hypophosphite. (i) Silver nitrate solution test (**IV, 31,** *1*), $BaCl_2$ solution test (**IV, 31,** *2*), $CuSO_4$ solution test (**IV, 31,** *4*), and Zn + dilute H_2SO_4 test (**IV, 31,** *8*).

Cyanate. (i) Dilute H_2SO_4 test (**IV, 9,** *1*). (ii) Cobalt acetate solution test (**IV, 9,** *5*). (iii) Copper sulphate-pyridine test (**IV, 9,** *6*).

Ferrocyanide. (i) Ferric chloride solution test (**IV, 11,** *3*). (ii) Ferrous sulphate solution test (**IV, 11,** *4*). (iii) Uranyl acetate solution test (**IV, 11,** *11*).

Ferricyanide. (i) Ferrous sulphate solution test (**IV, 12,** *3*). (ii) Ferric chloride solution test (**IV, 12,** *4*).

Thiocyanate. (i) Ferric chloride solution test; colour discharged by $HgCl_2$ solution or by NaF solution, but not by dilute HCl (**IV, 10,** *6*). (ii) Cobalt nitrate solution test (**IV, 10,** *7*). (iii) Copper sulphate-pyridine test (**IV, 10,** *9*).

Acetate. (i) Action of ethyl or of *iso*-amyl alcohol and concentrated H_2SO_4 (**IV, 35,** *3*), $AgNO_3$ solution test (**IV, 35,** *4*), and $FeCl_3$ solution test (**IV, 35,** *6*). (ii) Cacodyl oxide test (**IV, 35,** *7*). (iii) Indigo test (**IV, 35,** *9*).

Formate. (i) Mercuric chloride solution test (**IV, 36,** *7*) or $AgNO_3$ solution test (**IV, 36,** *4*), and $FeCl_3$ solution test (**IV, 36,** *6*). (ii) Mercuric formate test (**IV, 36,** *8*).

Oxalate. (i) Immediate precipitation with $CaCl_2$ solution in neutral solution; precipitate decolourises a dilute solution of $KMnO_4$ (**IV, 37,** *3, 4*). (ii) Resorcinol test (**IV, 37,** *5*).

Tartrate. (i) Resorcinol test (**IV, 38,** *6*). (ii) Copper hydroxide test (**IV, 38,** *7*).

Citrate. (i) Denigès' test (**IV, 39,** *5*). (ii) Cadmium chloride solution test (**IV, 39,** *4*), and negative results with resorcinol and copper hydroxide tests (**IV, 38,** *6, 7*).

Salicylate. (i) Violet colouration with $FeCl_3$ solution, discharged by mineral acids (**IV, 40,** *5*), and soda lime test (**IV, 40,** *7*). (ii) "Oil of winter green" test (**IV, 40,** *2*).

Benzoate. (i) Buff-coloured precipitate with $FeCl_3$ solution, soluble in dilute HCl with precipitation of benzoic acid (**IV, 41,** *1*). (ii) Dilute H_2SO_4 test (**IV, 41,** *2*), and no precipitate with $BaCl_2$ solution in neutral solution.

Succinate. (i) Light brown precipitate with $FeCl_3$ solution, soluble in dilute HCl, but no precipitation of acid occurs (**IV, 42,** *3*). (ii) Fluorescein test (**IV, 42,** *6*).

V, 19. B. ANALYSIS OF A LIQUID

(*1*) Observe the colour, odour, and any special physical properties.

(*2*) Test its reaction towards litmus paper.

(*a*) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.

(*b*) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, borates, sulphides, cyanides, hypochlorites, zincates, aluminates, silicates and peroxides of the alkali metals, *etc.*

(*c*) *The solution reacts acid*: this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to solutions of salts in acids.

(*3*) Evaporate a portion of the liquid to dryness on the water bath; carefully smell vapours evolved from time to time. If a solid residue remains, examine as described under A for solid and non-metallic substances (Section **V, 1**). If a liquid remains, evaporate cautiously on a wire gauze in the fume cupboard; a solid residue should be examined as already stated. If charring occurs, organic matter is present, and must be removed before testing for Group IIIA in the subsequent systematic analysis. If no residue remains, then the liquid consists of some volatile substance which may be water or water containing certain gases or volatile substances, such as CO_2, NH_3, SO_2, H_2S, HCl, HBr, HI, H_2O_2, $(NH_4)_2CO_3$, *etc.*, all of which can be readily detected by special tests. It is best to neutralise the solution with sodium carbonate and test for acid radicals (anions).

(*4*) If the solution reacts alkaline, the following tests should be performed:—

(*a*) *Peroxides* (*e.g.*, H_2O_2). (i) Heat a little of the solution with a few drops of cobalt nitrate solution; a black precipitate of a higher oxide of cobalt is obtained (sulphides and hypochlorites interfere and must be absent).

(ii) Add a little titanous sulphate or chloride solution, and carefully acidify with cold dilute sulphuric acid; a yellow colouration is obtained in the presence of hydrogen peroxide.

(iii) Add a little ferric chloride and potassium ferricyanide solutions; Prussian blue precipitate.

(*b*) *Hydroxides and carbonates.* Boil to decompose hydrogen peroxide, if present. Add a slight excess of barium chloride solution ; if the solution now reacts alkaline, hydroxyl ions are present. Filter off the precipitate, and examine for carbonate with dilute acid (see Section **IV, 2**, reaction *1*).

V, 20. C. ANALYSIS OF A METAL OR AN ALLOY

The analysis of a metal or of an alloy is simplified by the fact that no acid radicals or anions need be looked for. Many alloys contain small amounts of P, Si, C and S ; phosphorus is converted by the usual solution process into phosphate, and may be identified as such (Section **IV, 28**).

The alloy or metal should be in the form of borings, turnings or filings. About 1 gram is treated with 20 c.c. of concentrated nitric acid in a porcelain basin in the fume chamber, warmed gently until the evolution of red fumes ceases, and evaporated almost to dryness*. About 20 c.c. of water are then added, the mixture heated for a few minutes and filtered, if necessary.

Two cases may arise :—

1. *The metal or alloy dissolves completely.* Examine solution by Table XXIV (Section **V, 6.**), remembering that phosphate may be present and should be tested for.

2. *The metal or alloy does not dissolve completely.* The solution (*A*) is examined as in case 1. If the residue is black, it may be either carbon or gold and/or platinum. Test for carbon by igniting on a crucible lid ; carbon glows and burns. Gold and platinum dissolve in aqua regia (compare Sections **VII, 5** and **VII, 6.**)

If the residue is white, it may contain *inter alia* hydrated stannic oxide or antimony pentoxide, bismuth oxide, together with traces of copper, lead and iron, and is best analysed as outlined in the following table.

---

* The nitric acid will oxidise the P to H_3PO_4, S to H_2SO_4, As to H_3AsO_4, Sb to Sb_2O_5,xH_2O (converted by gentle heating into Sb_2O_4), Sn to SnO_2,xH_2O, and Si to gelatinous silicic acid.

Table XXXVIII.—Analysis of Portion of Alloy Insoluble in Concentrated Nitric Acid

Wash residue with water, and dry by heating in a crucible. Add 6 times its weight of an intimate mixture of equal parts of anhydrous Na_2CO_3 and sulphur, mix well, cover the crucible, and heat over a small flame until the excess of sulphur has burned off. This operation usually occupies about 20 minutes. Allow to cool and extract contents of the crucible with hot water, and filter.

<table>
<tr>
<td rowspan="2">Residue. May contain PbS, Bi_2S_3, CuS and FeS. Dissolve in hot dilute HNO_3, filter off any S, and evaporate almost to dryness. Dissolve in water and add to original solution <i>A</i>.</td>
<td colspan="2">Filtrate. May contain Na_2SnS_3, Na_3SbS_4,* Na_3AsS_4, Na_3PO_4 and, possibly, Na_2S. Acidify with dilute HCl (test with litmus paper), and filter.</td>
</tr>
<tr>
<td>Residue. May contain SnS_2, Sb_2S_5, As_2S_5 and S.
Examine by Tables XXX to XXXII (Section 134) for As, Sb and Sn.</td>
<td>Filtrate. Test for phosphate. Boil off H_2S, add excess of NH_4OH solution and then magnesia mixture. A white crystalline ppt. indicates phosphate present. Confirm.</td>
</tr>
</table>

The compositions of some of the common alloys are given in Table XXXIX; the chief constituents are listed in the order of their predominance.

Table XXXIX.—Composition of Alloys

Brasses	Cu, Zn, Sn, Pb
Bronzes	Cu, Sn, Zn, Pb
Phosphor bronzes	Cu, Sn, Pb, P
Solders	Sn, Pb, Bi
Pewter	Sn, Sb, Pb, Cu
Type metals	Pb, Sb, Sn
German silver	Cu, Ni, Zn
Monel metal	Ni, Cu
Constantan	Cu, Ni
Nichrome	Ni, Fe, Cr
Manganin	Cu, Mn, Ni
Wood's alloy	Bi, Pb, Sn, Cd
Rose's alloy	Bi, Pb, Sn

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* These are formed in accordance with the following equations:—

$$2SnO_2 + 2Na_2CO_3 + 9S = 2Na_2SnS_3 + 3SO_2 + 2CO_2.$$

$$2Sb_2O_4 + 6Na_2CO_3 + 23S = 4Na_3SbS_4 + 7SO_2 + 6CO_2.$$

V, 21. D. ANALYSIS OF INSOLUBLE SUBSTANCES

A substance which cannot be dissolved by concentrated acids (hydrochloric or nitric) or by aqua regia is described as "insoluble." Special methods for solution must therefore be employed, the actual process chosen depending largely upon the nature of the insoluble substance.

The most common insoluble substances encountered in qualitative analysis are :—

AgCl, AgBr, AgI, AgCN ;

$SrSO_4$, $BaSO_4$, $PbSO_4$;

the strongly ignited oxides Al_2O_3, Cr_2O_3, Fe_2O_3, SnO_2, Sb_2O_4, TiO_2 ;

fused $PbCrO_4$, and certain minerals, *e.g.*, CaF_2 (fluor spar), $FeCr_2O_4$ (chrome ironstone) ;

$Cu_2[Fe(CN)_6]$, $Zn_2[Fe(CN)_6]$, Prussian blue ;

SiO_2, and various silicates ; SnS_2 (mosaic gold) ; C and S.

The insoluble substance should be subjected to the tests enumerated below in the order given until it is brought into solution. (Some of these tests will have been carried out in the preliminary examination.) The substance should be in the form of a fine powder ; use an agate mortar, if necessary.

(1) Note colour and appearance.

The following substances are coloured :—Cr_2O_3 (green), Fe_2O_3 (dark red), SnS_2 (bronze), $PbCrO_4$ (brown), $Fe_4[Fe(CN)_6]_3$ (Prussian blue), $Cu_2[Fe(CN)_6]$ (dark brown), $FeCr_2O_4$ (dark grey), AgBr* (very pale yellow), AgI* (light yellow), C and S.

The remaining substances listed above are white or nearly so, but may be slightly coloured by traces of impurities ; the effect of the latter is less marked when the substance is in the form of a fine powder.

(2) Examine the effect of heat.

Heat a small quantity in a small crucible or upon platinum foil. Sulphur will melt to a yellow liquid, and burn with a blue flame with the production of sulphur dioxide (test with potassium dichromate paper).

Carbon will glow and burn away almost completely ; a light-coloured ash may remain. If the black substance is dropped in *very small quantities* into a little fused potassium nitrate contained in a hard glass tube, the oxidation will be more vigorous and some potassium carbonate will be formed. The residue will evolve carbon dioxide on treatment with dilute acids. Additional confirmation of carbon is obtained by heating an intimate mixture of the substance with dry cupric oxide in a hard glass tube; carbon dioxide will be evolved (test with lime water), and red metallic copper will remain.

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* The silver halides become violet on exposure to light.

$$2CuO + C = CO_2 + 2Cu.$$

The silver salts, AgCl, AgBr and AgI, will melt without further change; AgCN decomposes to give a residue of silver, and cyanogen gas is evolved.

Antimony oxide Sb_2O_4 melts to a yellow liquid.

(3) Heat with sodium carbonate upon charcoal.

The following observations may be made :—

(*a*) No metallic button is produced. This indicates the absence of Ag, Sn and Pb. Either moisten residue with a few drops of dilute hydrochloric acid and place in contact with lead acetate paper or extract with a little water and filter into freshly prepared sodium nitroprusside solution; a black stain or a transient violet colouration respectively indicates the presence of sulphide and therefore of *sulphate* in the original substance.

The test should be repeated with another portion of the original substance if a white residue is obtained. Add one or two drops of cobalt nitrate solution and heat again. A blue mass indicates *aluminium*.

(*b*) A metallic button or bead is obtained. The solubility of the bead in nitric acid and in hydrochloric acid is tested.

- (i) The bead dissolves in nitric acid forming a clear solution, and yielding a curdy, white precipitate of silver chloride, soluble in dilute ammonium hydroxide solution, upon the addition of a little hydrochloric acid. The presence of *silver* and the absence of tin is indicated.
- (ii) The bead gives a clear solution with hydrochloric acid, and the addition of mercuric chloride solution produces a white precipitate of mercurous chloride. With nitric acid, a white insoluble powder ("metastannic acid") is produced. This test indicates the presence of *tin* and the absence of silver.

(4) Heat with concentrated sulphuric acid.

(i) Escaping gas renders a drop of water upon a glass rod turbid. *Fluoride* is indicated.

(ii) Carbon monoxide evolved, which burns with a blue flame. *Ferrocyanide* is indicated.

(5) Heat upon a platinum wire in the reducing zone of the Bunsen flame.

This process will reduce any sulphate present to sulphide (as already indicated in test **3**). Upon moistening with dilute hydrochloric acid, the sulphide will be converted into the comparatively volatile chloride, and the usual flame test is applied. The presence of *barium* or of a mixture of *strontium and barium* will be indicated.

(6) Apply the microcosmic bead test.

If a skeleton bead is obtained, *silica* or a *silicate* is indicated. A negative result does not definitely prove that silica or a silicate is absent, as a skeleton is not always formed. The silicon tetrafluoride test should then be employed (Section **IV, 26,** reaction *6*).

Heat the bead in the reducing flame in order to test for *titanium*. If the bead is violet when cold (the colour is produced more readily by the addition of a minute speck of tin or of stannous chloride), the presence of titanium is indicated. If iron is also present, the bead will be coloured brownish-red in the reducing flame.

When titanium is found, it is best to fuse with potassium pyrosulphate in a silica or platinum crucible, and to extract the residue with *cold* water whereby a solution of titanic sulphate is obtained.

(7) Heat with sodium carbonate and potassium nitrate.

This test may be carried out in a loop of platinum wire or upon platinum foil or upon a piece of broken porcelain. If *chromium* is present, a yellow melt is produced. This should be dissolved in water, acidified with dilute acetic acid, and (a) silver nitrate solution added, when reddish-brown silver chromate is precipitated, (b) lead acetate solution added, when yellow lead chromate is precipitated, or (*c*) 1–2 c.c. of diphenylcarbazide reagent added, when a deep red colouration is produced.

(8) Boil with sodium hydroxide solution.

(i) Lead chromate dissolves:

$$PbCrO_4 + 4NaOH = Na_2CrO_4 + Na_2[PbO_2] + 2H_2O.$$

(ii) Prussian blue yields ferric hydroxide and sodium ferrocyanide (see under Iron, Sect. **III, 20,** reaction *5*)

(iii) Copper ferrocyanide yields copper oxide and sodium ferrocyanide.

(iv) Zinc ferrocyanide yields sodium zincate and sodium ferrocyanide, *i.e.*, it dissolves completely. The zinc is readily identified by passing hydrogen sulphide into the solution; the ferrocyanide (see Section **IV, 11**) is detected in the filtrate after acidifying and boiling off the hydrogen sulphide.

(v) Alumina and silica may dissolve, forming solutions of sodium aluminate and sodium silicate respectively.

(9) Heat with concentrated hydriodic acid.

The powdered substance (0·5 g.) should be heated to just below the boiling point with hydriodic acid, sp. gr. 1·7* (2·5 c.c.).

(i) Stannic oxide dissolves. A pink to red colouration is produced when the solution cools; the colouration disappears on warming to 90°–100° C. A yellow to orange sublimate of stannic iodide is frequently observed.

$$SnO_2 + 4HI \rightleftharpoons SnI_4 + 2H_2O.$$

Upon filtration and dilution, the tin may be precipitated with hydrogen sulphide.

(ii) The sulphates of lead, strontium and barium are gradually decomposed and hydrogen sulphide is evolved, which is identified by ammoniacal sodium nitroprusside paper (see under Sulphides, Section **IV, 6,** reaction *6*).

$$PbSO_4 + 11HI = H[PbI_3] + 4I_2 + H_2S + 4H_2O.$$

$$BaSO_4 + 10HI = BaI_2 + 4I_2 + H_2S + 4H_2O.$$

Upon filtration through a sintered glass crucible and dilution, golden yellow lead iodide is precipitated from lead sulphate.

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* Where colour reactions are to be observed, it is recommended that the hydriodic acid be decolourised by the addition of 1–2 per cent by volume of 50 per cent hypophosphorous acid or by warming with a little potassium hypophosphite.

Barium may be detected by the addition of dilute sulphuric acid, and strontium by sulphuric acid and ethyl alcohol.

(iii) The silver halides dissolve readily in the *cold*, owing to complex formation :

$$3AgI + HI = H[Ag_3I_4] ;$$

$$3AgX + 4HI = H[Ag_3I_4] + 3HX \quad (X = Cl \text{ or } Br).$$

Upon warming the solution, the hydrogen halides are expelled from solution with effervescence. When the solution is diluted, the complex iodo-argentous acid is decomposed and silver iodide is precipitated ; it is best, however, to expel the excess of hydriodic acid by evaporation before diluting with water. If lead sulphate was originally present, lead iodide will be precipitated on dilution ; this can be separated from silver iodide by extraction with ammonium acetate solution.

(iv) Calcium fluoride is attacked by the hot acid, hydrogen fluoride being evolved, which will etch glass :

$$CaF_2 + 2HI = CaI_2 + 2HF.$$

Upon dilution, neutralisation with ammonia solution and addition of ammonium oxalate solution, the calcium is precipitated as calcium oxalate.

PREPARING A SOLUTION

The above preliminary tests may supply valuable information as to the composition of the insoluble substance. In every case, the following methods of bringing the substance in solution for systematic analysis should be used.

(a) Removal of silver salts.

Warm with a concentrated solution of potassium cyanide. (If it dissolves completely, only AgCl, AgBr, AgI and AgCN are present.) Filter and reserve the residue *R* for subsequent treatment. Dilute the filtrate considerably and treat with hydrogen sulphide. Filter off any black precipitate (Ag_2S), wash, dissolve in hot dilute nitric acid, and add dilute hydrochloric acid. A white precipitate of silver chloride indicates the presence of *silver*.

If silver is found, the anion with which the metal was originally combined is determined by melting another portion of the original substance, immersing it in dilute sulphuric acid, placing a piece of zinc in contact with the acid and the fused mass, warming and allowing to stand for a few minutes. The silver salt is reduced to metallic silver, whilst the acid radicals (anions) are present in solution in the presence of zinc ions, *i.e.*, as zinc salts. Filter. Test a portion of the filtrate for the cyanide ion by adding sodium hydroxide solution until alkaline, followed by a little freshly prepared, concentrated ferrous sulphate solution. On gently warming the mixture, adding a few drops of ferric chloride solution, cooling and acidifying with concentrated hydrochloric acid a precipitate of Prussian blue will be formed if cyanide is present. The remainder of the filtrate is tested for chloride, bromide and iodide in the usual manner; the tests for mixtures of these anions are described in Section **IV, 44.**

(b) Sodium Carbonate Fusion.

The residue *R*, free from silver salts, or the original substance, if silver salts are absent, is mixed with 5–6 times its weight of pure, sulphate-free, anhydrous Na_2CO_3 or with a mixture of equal parts of Na_2CO_3 and K_2CO_3 (fusion mixture). The mixture is heated upon Pt foil or in a Ni crucible until a tranquil melt is obtained. (It may be necessary to heat over the blowpipe flame.) Allow to cool, extract the melt thoroughly by boiling it with water. Filter.

<table>
<tr>
<td colspan="2">Residue. Wash well, first with 5% Na_2CO_3 solution, and then with hot water. May contain <i>inter alia</i> $BaCO_3$, $SrCO_3$, $CaCO_3$, basic Pb carbonate, and unattacked CaF_2, SnO_2, Sb_2O_4, Al_2O_3, Fe_2O_3, etc.
Extract with dilute HNO_3, and filter.</td>
<td colspan="2">Filtrate. May contain Na_2CrO_4, $Na[AlO_2]$, $Na_2[SnO_3]$, Na_3AsO_4, NaF, Na_2SO_4, and the corresponding K salts if fusion mixture was employed. Acidify with concentrated HCl and evaporate to dryness in the fume cupboard. Triturate the dry mass with concentrated HCl, add water, warm, and filter.</td>
</tr>
<tr>
<td>Residue. If white, may contain CaF_2, SnO_2, Al_2O_3, SiO_2, <i>etc.</i>, which are incompletely attacked by Na_2CO_3. Fuse with NaOH in a Ni crucible*.
Allow to cool, extract with water, and filter. The filtrate may contain $Na_2[SnO_3]$, Na_2SiO_3 and $Na[AlO_2]$.
Test for Sn and Al.</td>
<td>Filtrate. Evaporate almost to dryness to remove HNO_3, add dilute HCl, and examine for metal ions by Table XXIV.</td>
<td>Residue. May contain SiO_2. Confirm by microcosmic bead test.</td>
<td>Filtrate. Test a portion for sulphate. Examine for metals of Groups II and III.</td>
</tr>
</table>

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* An alternative procedure is to use the Na_2CO_3–S fusion method already described under the analysis of metals and alloys (Section **V, 20,** Table XXXVIII).

Note. Lead sulphate and most lead salts, with the exception of the silicates, are soluble in concentrated ammonium acetate solution, and these may be removed in this way before the silver salts, if desired.

Metallic silicides and carborundum are rarely encountered in routine qualitative analysis. They are best brought into solution by fusion with sodium or potassium hydroxide in a silver crucible :

$$SiCu_2 + 2KOH + H_2O = K_2SiO_3 + 2Cu + H_2 ;$$

$$SiC + 4KOH + 2H_2O = K_2SiO_3 + K_2CO_3 + 4H_2.$$

During the fusion the liberated hydrogen catches fire forming water by combination with the oxygen of the air. Upon treating the melt with water, the soluble potassium silicate, etc., is extracted.

Carborundum when in the form of a fine powder is readily decomposed by fusion with potassium carbonate in a platinum crucible. Upon removing the cover of the crucible the blue flame of burning carbon monoxide may be seen.

$$SiC + 3K_2CO_3 = K_2SiO_3 + 2K_2O + 4CO.$$

CHAPTER VI

MODIFICATION OF THE SYSTEMATIC ANALYSIS WHEN ORGANIC ACIDS, SILICATES, BORATES, FLUORIDES AND PHOSPHATES ARE PRESENT

REFERENCE has already been made in Chapter V, Tables XXIV and XXV, to the modification of the analysis after Group II necessitated by the presence of various interfering acid radicals. It is the express purpose of this Chapter to discuss this subject in greater detail in order that the student may understand the reason for each operation, and also to indicate alternative procedures whereby some of the interfering radicals may be removed.

The interfering acid radicals may be divided into two main groups :—

(i) Those which, when present in solution, combine with various metals to form stable complex ions (compare Section **I, 20**) ; this may result in the failure of these metals to precipitate with the usual group reagent. To this class belong such organic acids as oxalic, citric and tartaric acids, and also hydroxy compounds, such as sugar and starch. In their presence, iron, chromium and aluminium are either incompletely precipitated or not precipitated at all by ammonium chloride and ammonium hydroxide solution.

(ii) Those which, under certain conditions, form insoluble compounds with some of the metals of the later groups. It is conceivable, therefore, that under conditions which result in the precipitation of the Group IIIA metals, metals of the subsequent groups will also be precipitated in consequence of the formation of compounds which are insoluble or sparingly soluble in the presence of ammonium chloride and ammonium hydroxide solution. The most important of these acid radicals are oxalates, tartrates, citrates, borates, fluorides and phosphates. Silicates are included with these owing to the precipitation of gelatinous silicic acid by ammonium chloride and ammonium hydroxide solution (see under Silicates, Section **IV, 26,** reaction *2*).

Reference to a table of solubilities will show :

(*a*) That the oxalates, tartrates and citrates of most of the metals of Groups IIIA, IIIB and IV and of magnesium are either insoluble or difficultly soluble in water. (It should be noted that most oxalates and tartrates, with the exception of those of calcium, strontium and barium, form soluble complex salts with alkali oxalates and alkali tartrates respectively ; compare (i) above.)

(*b*) That the borates of the metals of Groups IIIA, IIIB and IV are insoluble in water ; magnesium borate is sparingly soluble. (Some of these are, however, soluble in ammonium chloride solution.)

(*c*) That the fluorides of calcium and magnesium are insoluble, and those of nickel, cobalt, strontium and barium are sparingly soluble in water.

(*d*) That the phosphates of the metals of Groups IIIA, IIIB, IV and of magnesium are insoluble in water.

It is evident that in the presence of these acids, Group IIIA metals cannot be separated from those of the remaining groups by the addition of the customary group reagent, NH_4Cl and NH_4OH solution. The usual scheme of systematic analysis is therefore modified when any or all of these anions are present before proceeding to the precipitation of Group IIIA.

The presence of some of these anions will have been indicated in the preliminary tests. Organic acids are revealed in the dry tests, and particularly by the action of concentrated sulphuric acid. In view of the common occurrence of oxalates and the somewhat indecisive indications of the preliminary tests, it is recommended that this radical be tested for in a portion of the filtrate from Group II, from which all the hydrogen sulphide has been expelled by boiling. This is most simply carried out by adding 2 c.c. of $CaCl_2$ solution and 2 c.c. of $Na.C_2H_3O_2$ solution to 2–3 c.c. of the solution ; if a *crystalline* precipitate forms (the precipitate should not be confused with *gelatinous* CaF_2), filter, wash, dissolve in a little hot dilute H_2SO_4, filter, and add 2–3 drops of dilute $KMnO_4$ solution to the filtrate. If the colour of the $KMnO_4$ solution is discharged, an *oxalate* is present.

The presence of *fluoride* is indicated in the preliminary treatment with concentrated sulphuric acid ; a moistened glass rod introduced into the tube becomes covered with a film of gelatinous silicic acid.

The detection of *borate* is provided for in the simple preliminary tests of Section **V, 3.** Alternatively, it may be tested for after the precipitation of Group II.

The presence of *phosphate* is always tested for in the Group II filtrate, from which all the H_2S has been expelled. To 2–3 c.c. of the solution, add 3 c.c. of HNO_3 and 10 c.c. of ammonium molybdate solution, and warm to a temperature not exceeding 40°. The production of a bright yellow precipitate proves the presence of a phosphate (Section **IV, 28,** reaction *4*).

VI, 1. PROCEDURE FOR THE REMOVAL OF INTERFERING ACIDS IN SYSTEMATIC QUALITATIVE ANALYSIS

The acids are removed in the following order :—

1. **Organic Acids.** The filtrate from Group II is evaporated to dryness, when some carbon may be liberated and the organic acids decomposed. By repeated evaporation with concentrated HNO_3, the black residue is completely oxidised. The residue must not be heated too strongly as Fe_2O_3, Cr_2O_3 and Al_2O_3 may be rendered very difficultly soluble in HCl.

2. **Borates and fluorides.** The residue from *1* is repeatedly evaporated almost to dryness with concentrated HCl ; the HF volatilises with the HCl and the B_2O_3 volatilises in the steam.

If borate is present and fluoride is absent, the former may be removed by repeated evaporation to dryness with a mixture of methyl alcohol (inflammable !) and concentrated HCl. The borate slowly volatilises as methyl borate, $(CH_3)_3BO_3$.

3. **Silicates.** The evaporation with concentrated HCl converts silicates into an insoluble form of SiO_2. Hence by complete evaporation to dryness with a further quantity of concentrated HCl, extraction with water or dilute HCl, and filtration, the silicate is completely eliminated.

4. **Phosphates.** There are several methods for the removal of phosphoric acid ; one of these, the basic acetate method, has already been outlined in Table XXV. This and other available methods will now be described in some detail.

VI, 2. ANALYTICAL PROCEDURE IN THE PRESENCE OF PHOSPHATES. "PHOSPHATE SEPARATIONS"

The various methods which have been proposed for the removal of the interfering phosphate ion in qualitative analysis are all based upon precipitation processes. Six of these, *viz.*, (*a*) the basic acetate method, (*b*) the ferric chloride method, (*c*) the tin method, (*d*) the stannic chloride method, (*e*) the formate buffer method and (*f*) the zirconium phosphate method will be described.
and (*e*) the formate buffer method will be described.

The filtrate from Group II is boiled to remove H_2S, about 1 c.c. of concentrated HNO_3 added and the solution boiled for several minutes to oxidise completely any iron present*. (About 2 c.c. of the solution is tested for Fe by adding a few drops of $K_4[Fe(CN)_6]$ solution; the production of a blue precipitate indicates the presence of Fe. The original solution or substance must be tested for Fe^{++} or Fe^{+++} as in Section **III, 20.**) Test another portion of the solution for phosphate as follows: to 2–3 c.c. of the solution add 1–2 c.c. of concentrated HNO_3, and 5–10 c.c. of ammonium molybdate solution and warm (not above 40°); the formation of a bright yellow precipitate indicates the presence of a phosphate.

If the solution being analysed contains the metals of Groups IIIB and IV and also Mg, then the Group IIIA reagent, NH_4Cl and NH_4OH solution, may precipitate, in addition to the phosphates and hydroxides of Fe, Al and Cr, the phosphates of Ni, Co, Zn, Mn, Ba, Sr, Ca and Mg, since these phosphates are either sparingly soluble or insoluble under these experimental conditions (ammoniacal solution). It is evident that phosphoric acid must be removed before the analysis for the metals of Groups IIIB, IV and Mg can be attempted.

(a) The basic acetate method.—The phosphates of Fe, Al and Cr are insoluble in dilute acetic acid in the presence of excess of acetate ions—otherwise expressed, these phosphates are insoluble in acetic acid buffered by alkali acetate (see Buffer Solutions, Section **I, 39**); the phosphates of the metals of the $(NH_4)_2S$ and $(NH_4)_2CO_3$ groups and of Mg are appreciably soluble in this reagent†. If a solution of ferric acetate is considerably diluted and boiled, the iron is quantitatively precipitated as the brown basic acetate.

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* This procedure is, of course, unnecessary if organic acids are present and have been eliminated as described in Section **VI, 1.**

† $CrPO_4$ is slightly soluble in cold dilute acetic acid, but is re-precipitated on boiling.

$$Fe(C_2H_3O_2)_3 + 2H_2O = Fe(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

Aluminium acetate solution behaves similarly, basic aluminium acetate being precipitated on dilution and boiling; here it is advisable to filter the solution hot as a partial reversal of the reaction may occur on cooling.

$$Al(C_2H_3O_2)_3 + 2H_2O \rightleftharpoons Al(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

Chromium acetate solution, on the other hand, does not form a basic acetate under these conditions, and is therefore not precipitated on dilution and boiling. If, however, considerable quantities of Fe and Al are present, Cr is almost completely precipitated with the Fe and Al either as the basic acetate or as an adsorption compound. In the presence of excess of Cr, incomplete precipitation of the Cr occurs, and the filtrate may contain Fe and Al with Cr ; the basic acetate method of separation then becomes somewhat uncertain.

At this stage, the student is recommended to carry out the following simple experiments ; this will help him to appreciate the processes involved, and also assist to impress them upon his memory.

(i) Add sodium phosphate solution to ammoniacal calcium chloride solution ; calcium phosphate is precipitated. Add dilute hydrochloric acid until the precipitate is just dissolved, and render alkaline with ammonium hydroxide solution ; calcium phosphate is re-precipitated.

(ii) Dissolve the precipitate of calcium phosphate in the minimum quantity of dilute hydrochloric acid, dilute largely, and add 5–10 c.c. of saturated ammonium acetate solution. No precipitate is formed.

This is because any free hydrochloric acid reacts with the ammonium acetate, liberating acetic acid, and calcium phosphate is soluble in dilute acetic acid.

(iii) Repeat experiment (i) with a solution of aluminium sulphate ; a white precipitate of aluminium phosphate is produced. This is soluble in dilute hydrochloric acid, and is re-precipitated by ammonium hydroxide solution.

(iv) Dissolve the aluminium phosphate precipitate in dilute hydrochloric acid, add excess of ammonium acetate solution and boil. A gelatinous white precipitate of aluminium phosphate, containing some basic aluminium acetate, is produced. The phosphates and basic acetates of the metals of Group IIIA are insoluble in hot dilute acetic acid.

(v) Repeat experiments (iii) and (iv) with a solution of ferric chloride. Similar results are obtained.

(vi) Add 0·5–1 c.c. of ferric chloride solution * to 100 c.c. of water contained in a beaker, and then add 1 c.c. of saturated ammonium acetate solution. A red colouration, due to ferric acetate, is produced. Boil the solution for several minutes. Observe the formation of reddish-brown basic ferric acetate. Filter; the filtrate is free from iron (test with potassium ferrocyanide solution).

(vii) Dissolve a little calcium phosphate in dilute acetic acid, dilute largely, and add ammonium acetate solution as in (ii). Add ferric chloride solution * drop by drop to the clear solution. Yellowish-white ferric phosphate will be precipitated since it is insoluble in acetic acid; when precipitation is complete, further addition of ferric chloride solution will result in the formation of ferric acetate, the presence of which will be indicated by the reddening of the precipitate. Dilute considerably and boil for several minutes. The ferric acetate will be converted into insoluble basic ferric acetate, and upon filtering the solution, the filtrate will be colourless and free from phosphate and iron.

The reactions which take place may be represented as follows :—

$$Ca_3(PO_4)_2 + 6HCl = 3CaCl_2 + 2H_3PO_4\,;$$

$$H_3PO_4 + 3NH_4.C_2H_3O_2 = (NH_4)_3PO_4 + 3H.C_2H_3O_2\,;$$

$$(NH_4)_3PO_4 + FeCl_3 = FePO_4 + 3NH_4Cl\,;$$

$$FeCl_3 + 3NH_4.C_2H_3O_2 = Fe(C_2H_3O_2)_3 + 3NH_4Cl\,;$$

$$Fe(C_2H_3O_2)_3 + 2H_2O = Fe(OH)_2.C_2H_3O_2 + 2H.C_2H_3O_2.$$

(viii) Add excess of ferric chloride solution * to 0·5 c.c. of ammonium phosphate solution and shake. The precipitate of ferric phosphate dissolves slowly. Now add excess of ammonium acetate solution to the solution; the latter acquires the red colour characteristic of ferric acetate, but no ferric phosphate is precipitated. This is because ferric phosphate is soluble both in ferric chloride solution and in ferric acetate solution. Boiling of the above red solution results in only partial precipitation of the iron, and hence the method of separation would be unsatisfactory under these conditions, *i.e.*, in the presence of excess of ferric chloride solution. If a portion of the solution be considerably diluted, then ammonium phosphate solution may be added until the turbid liquid just remains red ; this is indicative of the presence of only a *slight* excess of ferric chloride. (The addition of too much ammonium phosphate solution leads to the formation of a yellowish precipitate of ferric phosphate ; ferric chloride solution may then be added until the precipitate just begins to redden.) Subsequent boiling of the solution results in complete precipitation, and the filtrate will be free from iron and phosphate.

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* When " $FeCl_3$ solution " is employed in this Chapter, " neutral $FeCl_3$ solution " is to be understood; for preparation, see *Note 2* to Table XXV.

The conclusion to be drawn from experiment (viii) is that if iron is initially present in the solution, then the amount of phosphate present must be at least equivalent to it in order that separation of the latter may be satisfactory. If this is not the case, ammonium phosphate solution must be added in the manner described above.

The procedure by the basic acetate method, when a portion of the solution gives the test for a phosphate and a precipitate is obtained with ammonium chloride and ammonium hydroxide solution, is given in Table XL. Most of this has been given in Table XXV in Chapter V, but is presented fully here. It is considered that this partial duplication coupled with the performance of experiments (i) to (viii), will help the student to master this seemingly difficult subject.

In a modification of this method, which is frequently employed, the ammonium acetate and $FeCl_3$ treatments are combined and are carried out consecutively without previous filtration. The precipitate (*D*) thus obtained after dilution and boiling consists of the residues (*A*) and (*B*) in the above Table and may contain the phosphates and basic acetates of Fe, Al and Cr. It should be washed and transferred to an evaporating basin containing 10–15 c.c. of cold water, treated with 1–1·5 grams of Na_2O_2 in small portions, heated to boiling and filtered. The precipitate, containing $FePO_4$ and $Fe(OH)_3$, is rejected, and the filtrate tested for Al and Cr according to Table XXXIII.

The filtrate from (*D*) is examined as detailed from (*C*) onwards in Table XL.

The theoretical basis of the basic acetate method may be summarised as follows :—

(1) $FePO_4$, $AlPO_4$ and, to a lesser extent, $CrPO_4$ are insoluble in warm dilute acetic acid containing excess of ammonium acetate ; the phosphates of the metals of Groups IIIB and IV and of Mg are soluble.

Table XL.—Phosphate Separation by the Basic Acetate Method

The ppt. produced by the action of NH_4Cl and a slight excess of NH_4OH solution is dissolved in the *minimum* volume of dilute HCl. Test about 1 c.c. for Fe by the addition of $K_4[Fe(CN)_6]$ or NH_4CNS solution. To the main volume of the cold solution, add dilute NH_4OH solution drop by drop until a faint permanent ppt. is just obtained or until the solution is just alkaline (test with litmus paper). Then add 2–3 c.c. of dilute acetic acid (1 : 1), 4–5 c.c. of saturated ammonium acetate solution and boil. If a ppt. forms, add ammonium acetate solution until precipitation appears complete. Boil and filter hot.

Residue. (*A*) May contain phosphates and possibly basic acetates of Fe, Al and Cr. **Group IIIA present.** Examine for Al and Cr by Group Separation Table XXXIII.

Filtrate. If the solution is not red, add $FeCl_3$ solution ‡ drop by drop until the solution just acquires a red colour.* Dilute to 150 c.c., boil for 2–3 minutes, and filter hot.

If the solution becomes red when ammonium acetate solution is added and iron is present, there is enough Fe present to combine with all the phosphoric acid †. Dilute to 150 c.c., boil for 2–3 minutes, and filter hot.

Residue. (*B*) $FePO_4$ and some basic iron acetate. Reject.

Filtrate. (*C*) Concentrate to 20–30 c.c., add 0·5 gram of NH_4Cl, and NH_4OH solution in slight excess. Filter, if necessary.

Residue. Examine for Al and Cr, if not previously tested for.

Filtrate. Examine for Groups IIIB, IV, and Mg as given in General Table XXIV.

(2) The addition of ammonium acetate solution to a solution containing Fe, Al and Cr yields the acetates of these metals; upon boiling the diluted solutions, the basic acetates of Fe and Al are almost completely precipitated, but the precipitation of Cr depends upon the relative quantities of Fe and Al present {see discussion at the beginning of method (**a**) }.

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* If the colour of the solution cannot be seen owing to the formation of a precipitate or the presence of coloured ions, filter off a small portion of the mixture and render the filtrate alkaline with ammonium hydroxide solution. If a light coloured ppt. is obtained, more $FeCl_3$ solution should be added slowly to the main solution with stirring until a similar test gives a reddish-brown ppt., showing that ferric ion is present in excess.

† See note to experiment (viii).

‡ "Neutral" $FeCl_3$ solution must be used; for preparation, see *Note 2* to Table XXV.

(3) The removal of the excess of phosphate ions is carried out by the addition of ferric ions ($FeCl_3$), unless these be already present. The advantages attending the use of $FeCl_3$ solution are :—(i) $FePO_4$ is the least soluble phosphate which may be precipitated in acetic acid solution, (ii) it is easy to test for Fe^{+++} in the filtrate from Group II, and (iii) the excess of Fe^{+++} ions can be readily removed, since ferric acetate is considerably hydrolysed on dilution and boiling, and the excess of iron is precipitated as basic ferric acetate.

(b) **The ferric chloride method.**—This method utilises some of the reactions employed in the basic acetate process, particularly the insolubility in acetic acid of the phosphates of the metals of Group IIIA and the solubility, in this reagent, of the phosphates of the metals of the succeeding groups. The method involves the precipitation in acetic acid solution of the metals of Group IIIA as phosphates by the addition of excess of ammonium phosphate solution. The excess of phosphate is removed from the filtrate by the addition of $FeCl_3$ solution, hence the name "ferric chloride method." The basic acetate procedure in which the addition of ammonium acetate and $FeCl_3$ solutions are combined is sometimes also termed the "ferric chloride method." It is, however, preferable to restrict the latter name to the processes just outlined and to be described in detail below, and to retain the term "basic acetate method" to the procedures or simple modifications involving the use of comparatively large quantities of alkali acetates in which no phosphates are actually added.

The experimental details are collected in Table XLI.

(c) **The metallic tin method.**—This method depends upon the following facts :—

(1) "Metastannic acid" is formed when tin is warmed with concentrated nitric acid ; this precipitates or adsorbs phosphate ions, possibly as stannic phosphate.

(2) "Metastannic acid" is somewhat soluble in hydrochloric acid, and hence the latter must be removed by evaporation with nitric acid.

The experimental procedure is as follows. Evaporate the filtrate from Group II, after, of course, testing for phosphate and precipitation with ammonium chloride and ammonium hydroxide solution, to about 2 c.c. Add 10–15 c.c. of concentrated nitric acid, and evaporate just to dryness. This will remove hydrochloric acid. Add 15 c.c. of concentrated

Table XLI.—Phosphate Separation by the Ferric Chloride Method

<table>
<tr><td colspan="3">Boil off the H_2S from the Group II filtrate ; add 1–2 c.c. of concentrated HNO_3 to oxidise any ferrous salt to the ferric state. Test a portion of the solution by adding NH_4Cl and a slight excess of NH_4OH solution ; if a precipitate is obtained, proceed as follows with the remainder of the solution. Add NH_4OH solution slowly until a ppt. just persists on shaking. Add 2–3 c.c. of dilute acetic acid (1 : 1), 3–4 c.c. of saturated ammonium acetate solution, and then $(NH_4)_2HPO_4$ solution until precipitation appears to be complete (Determine this by filtering, and testing a small portion of the filtrate with the reagent.) Filter and wash.</td></tr>
<tr><td rowspan="3">Residue. May contain $FePO_4$, $AlPO_4$ and $CrPO_4$. Group IIIA present. Examine by Group Separation Table XXXIII*.</td><td colspan="2">Filtrate. Add 5 c.c. of saturated ammonium acetate solution, then neutral $FeCl_3$ solution drop by drop, with shaking, until reddish tinge <i>just</i> appears. Filter.</td></tr>
<tr><td rowspan="2">Residue. $FePO_4$. Reject.</td><td>Filtrate. Warm, add 0·5–1 gram of NH_4Cl, then NH_4OH solution in slight excess, and filter.</td></tr>
<tr><td><table><tr><td>Residue. May contain $Fe(OH)_3$ and possibly $Cr(OH)_3$. Test for Cr. if not previously identified.</td><td>Filtrate. Examine for Groups IIIB, IV and V as given in General Table XXIV.</td></tr></table></td></tr>
</table>

nitric acid, and then 1·5 gram of tin (analytical reagent or equivalent purity) in small portions. Heat the mixture to boiling and evaporate over a small flame to about 1–2 c.c. (*Note*. This mixture bumps very easily and must be watched during the evaporation.) Add 20–30 c.c. of water, stir well and filter (preferably through a fluted filter paper). The filtrate should be free from phosphate ; if this is not the case, the process must be repeated. The filtrate should be treated to remove traces of lead and copper, which may be present in the tin ; this is carried out in the customary manner, *viz.*, evaporating almost to dryness to remove the nitric acid, adding dilute hydrochloric acid, and passing hydrogen sulphide into the solution. After boiling off the hydrogen sulphide, the solution is analysed for Groups IIIA to V in the usual manner.

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* The "aluminon" test may not be satisfactory in the presence of phosphates. See under Aluminium, Section **III, 21,** reaction 7.

(d) **The stannic chloride method.**—It has been found that a freshly prepared solution of stannic chloride removes phosphates from solution far more readily than the " metastannic acid " formed in (c). It is highly probable that it is removed in the form of stannic phosphate $Sn_3(PO_4)_2$; an alternative view is that an adsorption complex of H_3PO_4 and SnO_2,xH_2O is formed. Difficulty in filtration of the precipitate is encountered when small amounts of phosphates are present ; in the latter case, it is recommended that more phosphate, as $(NH_4)_2HPO_4$, be added to the solution before filtration.

The experimental procedure is as follows. The filtrate from Group II, after boiling to remove hydrogen sulphide, and diluting to 50 c.c., is treated with 5 c.c. of 5% $(NH_4)_2HPO_4$ solution (if necessary), and ammonium hydroxide solution slowly added until the precipitate which forms does not completely dissolve on shaking ; the solution is then neutralised with dilute hydrochloric acid (1 : 1 ; about 1–2 c.c.). The resultant solution is heated to boiling, and 3 c.c. of stannic chloride solution (prepared by dissolving 5 grams of the crystallised salt in 5 c.c. of cold water) added. A small portion is filtered and tested for phosphate with ammonium molybdate solution and nitric acid. If the test is positive, a further 1 c.c. of stannic chloride solution is added, and the process is repeated until the phosphate test is negative. **Filter** (preferably on a Buchner funnel provided with several filter papers), and wash. Reject the precipitate. Add 3 c.c. of dilute hydrochloric acid to the filtrate, precipitate the tin as stannic sulphide with hydrogen sulphide, filter and discard the precipitate ; analyse the filtrate for Groups IIIA to V in accordance with Table XXIV.

(e) **The formate buffer method.**—This method is due to T. B. Smith (1933). Slight modifications have been introduced which experience has shown to possess definite advantages. Separations are effected, as far as possible, in acid solution ; the necessity for removing the phosphate radical is thus avoided.

The filtrate from Group II, after removal of hydrogen sulphide, etc., is treated with ammonium chloride and ammonium hydroxide solution in the usual manner, followed by an excess of diammonium hydrogen phosphate solution. The phosphates of the metals of Groups IIIA, IIIB, IV and of Mg are therefore precipitated. These are separated as described in the following table.

TABLE XLII.—Phosphate Separation by the Formate Buffer Method.

Dissolve a small portion of the ppt. in dilute HNO_3, cool, and add 1 gram of $NaBiO_3$. Shake. Purple colouration (filter, if necessary) indicates **Mn present** (1).

Dissolve remainder of the ppt. in dilute HCl, dilute to *ca.* 60 c.c., and adjust to *p*H of approx. 3 by the addition of NH_4OH solution and the use of methyl violet as an external indicator. Add 10 c.c. of the formate buffer solution. Boil, and slowly add 10 c.c. of $8N$-$(NH_4)_2SO_4$ solution (2). Filter.

Residue. May contain $FePO_4$, $AlPO_4$, $CrPO_4$, $BaSO_4$ and $SrSO_4$. Suspend ppt. in water containing 1–2 g. of Na_2SO_4 (to reduce solubility of $SrSO_4$). Add 2 g. of Na_2O_2 portion-wise; boil, cool, and filter.

Residue. May contain $Fe(OH)_3$, $BaSO_4$ and $SrSO_4$. Boil with just sufficient dilute H_2SO_4 to dissolve the $Fe(OH)_3$. Filter.

Residue. May contain $BaSO_4$ and $SrSO_4$. Boil with conc. Na_2CO_3 solution (10 g. of anhydrous Na_2CO_3 in 50 c.c. of water). Filter and wash. Test residue for **Sr** and **Ba** (Table XXXV).

Filtrate. Test for Fe with $K_4[Fe(CN)_6]$ solution. Blue ppt. **Fe present.**

Filtrate. May contain Na_2CrO_4 and $Na_2[AlO_2$ Test for **Cr** and **Al** (3) (Table XXXIII)

Filtrate. Pass H_2S into the boiling solution. Filter.

Residue. White; ZnS. Confirm by Rinmann's green test. **Zn present.** If ppt. is dark, apply Table XXXIV and test for **Zn.**

Filtrate. Concentrate to 15–20 c.c.; add 15 c.c. of $0{\cdot}5N$-$(NH_4)_2C_2O_4$ solution. Allow to stand at least 5 minutes. Filter.

Residue. May contain CaC_2O_4. Ignite ppt. upon broken porcelain or upon Pt foil; dissolve residue in $2N$ acetic acid, filter, and treat filtrate with an equal volume of $0{\cdot}25N$-NaF solution, and boil. White turbidity or ppt. (CaF_2). **Ca present** (4).

Filtrate. Divide into 3 parts.

(i) Test for **Co** with α-nitroso-β-naphthol reagent (Section **III, 24,** *7*) or with the ammonium thiocyanate reagent (Section **III, 24,** *6*).

(ii) Test for **Ni** with dimethyl glyoxime reagent (Section **III, 25,** *8*).

(iii) Test for **Mg** with the "magneson" reagent (5) (Section **III, 33,** *8*).

Notes.

(1) Alternatively, the potassium periodate test (Section **III, 26**, *7*) may be used.

(2) The phosphates of Fe, Al and Cr are quantitatively precipitated at *p*H of about 3. This acidity is obtained by the use of the methyl violet indicator (*p*H range—0·1–3·2 ; colour change—yellow to violet) and the formate buffer solution. If the indicator is not available, ammonium hydroxide solution is added until a slight turbidity forms, followed by 20 c.c. of the formate buffer solution.

The combined precipitation of the phosphates of Group IIIA and of $SrSO_4$ + $BaSO_4$ avoids errors due to adsorption and to the solubility of $SrSO_4$.

(3) Use the perchromic acid test (Sect. **IV, 33,** *4*) or the diphenylcarbazide test (Sect. **IV, 33,** *10*) for chromate. The solution may contain much PO_4^{---} ion, and this will interfere with the lead acetate test.

(4) Oxalates of Co, Ni, Mn and Mg may be partially precipitated here. The fluoride test is not interfered with by these metals.

(5) If Co, Ni or Mn are present, they must be removed by precipitation as sulphides with ammonium chloride, ammonium hydroxide and ammonium sulphide solutions before applying the " magneson " test.

The procedure is then modified as follows: Add ammonium chloride, ammonium hydroxide and ammonium sulphides solutions, filter off the precipitated sulphides, and evaporate the filtrate to dryness to remove ammonium salts. Dissolve the residue in a little dilute hydrochloric acid, add a few drops of the " magneson " reagent, followed by sodium hydroxide solution until strongly alkaline. A blue colouration or precipitate indicates the presence of Mg.

SOLUTIONS REQUIRED.

Formate buffer solution.—Dissolve 57 grams of sodium formate H.COONa and 85 c.c. of 23·5*N* formic acid H.COOH (*d* 1·200) in water and dilute to 1 litre.

8*N-Ammonium sulphate solution.*—Dissolve 528 grams of ammonium sulphate $(NH_4)_2SO_4$ in water and dilute to 1 litre.

2*N-Acetic acid solution.*—Dissolve 115 c.c. of glacial acetic acid CH_3.COOH in water and dilute to 1 litre.

0·5*N-Ammonium oxalate solution.*—Dissolve 35·5 grams of ammonium oxalate $(NH_4)_2C_2O_4,H_2O$ in water and dilute to 1 litre.

0·25*N-Sodium fluoride solution.*—Dissolve 10·5 grams of sodium fluoride in water and dilute to 1 litre.

(f). The zirconium phosphate method.—Phosphate ions are practically completely precipitated by excess of zirconyl chloride $ZrOCl_2$ as white zirconium phosphate $Zr(HPO_4)_2$ from solutions which are 0·3–1*N* in hydrochloric acid. The excess of zirconium ions is removed by adding ammonia solution and boiling for a short time; the precipitated zirconium hydroxide $Zr(OH)_4$ (or $ZrO(OH)_2$) is then insoluble in dilute hydrochloric acid (compare Zirconium, Section **VII, 13,** reaction *2*). The disadvantage of the method for use on a macro-scale is that zirconium salts are expensive.

Concentrate the filtrate from Group II to remove hydrogen sulphide. Test small portions (*a*) for phosphate with ammonium molybdate solution and nitric acid and (*b*) for the presence of Groups IIIA, IIIB, IV or magnesium by the addition of ammonium chloride and ammonia solution. If both tests are positive, proceed as follows.

Add 2 g. of solid ammonium chloride, and then 5–10 c.c. of zirconyl chloride solution (1) dropwise and with vigorous stirring. Add 0·2 g. of finely-ground asbestos or one Whatman accelerator (compare Section **I, 43**), render alkaline with ammonia solution and boil for 3–5 minutes. Neutralise with dilute hydrochloric acid and add 10 c.c. of 2*N*-hydrochloric acid. Boil again for some minutes. Filter hot, preferably through a small Buchner funnel provided with 3–4 filter papers. The filtrate should be clear; refilter if necessary, and test a portion of the clear filtrate for phosphate (2). Analyse the filtrate, which contains traces of zirconium, for Groups IIIA–V in accordance with Table XXIV.

Notes. (1). The **zirconyl chloride reagent** is prepared by dissolving 17·7 g. of $ZrOCl_2,8H_2O$ in 100 c.c. of water. Ten c.c. of this solution will precipitate 1·000 g. of PO_4^{---}

(2). To (say) 5 c.c. of the filtrate add 2 c.c. of concentrated nitric acid and evaporate just to dryness to remove hydrochloric acid, which interferes with the molybdate test for phosphate. Add 2 c.c. of water, 1 c.c. of concentrated nitric acid and warm, if necessary, to effect solution. Add 3 c.c. of ammonium molybdate reagent and warm (not above 50°C). A yellow precipitate indicates the presence of phosphate.

An alternative experimental procedure employs an **acid solution of zirconium nitrate*** and is given in tabular form below.

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* J. Newton Friend, R. H. Vallance and H. J. G. Challis (1940).

Boil the filtrate from Group II until free from H_2S, and add a few drops of concentrated HNO_3. Test small portions for phosphate and for the presence of Groups III–IV and magnesium as described above. Add an acid solution of zirconium nitrate‡ dropwise until further precipitation ceases. Warm and filter off the precipitate of zirconium phosphate. [The addition of about 0·2 g. of finely-ground asbestos or of one Whatman accelerator facilitates filtration.]

Residue. Zirconium phosphate. Reject.

Filtrate. Test if all phosphate precipitated by addition of a drop of zirconium nitrate solution : if no ppt. forms, all the phosphate has been removed. Add 1–2 grams of solid NH_4Cl, heat to boiling, and add a slight excess of NH_4OH solution (*i.e.*, until the odour of ammonia is permanent) to the boiling solution, boil for several minutes, and filter.

Residue. Contains excess of Zr, with any Fe, Al or Cr originally present ; may also contain some Mn. Boil with excess of NaOH solution, dilute somewhat, and filter.

Residue. If brown, contains Fe. Transfer to a dish with a little water, add about 1 g. of Na_2O_2 portionwise (caution!), boil for 5 minutes and filter.

Residue. Extract with dilute HCl, and test extract with $K_4[Fe(CN)_6]$ solution. Blue ppt. **Fe present.** Test a portion for Mn as in Table **V, 13.**

Filtrate. May contain Na_2CrO_4. If colourless, Cr is absent and need not be further tested for. If yellow, acidify with acetic acid, and add lead acetate solution. Yellow ppt. of $PbCrO_4$. **Cr present.**

Filtrate. May contain $NaAlO_2$. Just acidify with dilute HCl, add NH_4OH solution in slight excess, and heat to boiling. White gelatinous ppt. **Al present.** Confirm by Thenard's blue test.

Filtrate. May contain members of Groups IIIB–V. Proceed as in Table **V, 6.**

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‡ Solutions of zirconium nitrate often contain aluminium. It is recommended that the zirconium nitrate solution be boiled with excess of sodium hydroxide solution, the precipitate washed repeatedly by decantation, and allowed to stand overnight. The suspension is then dissolved by warming with half its volume of 1 : 1-nitric acid, and the resulting solution is then ready for use.

CHAPTER VII

REACTIONS OF SOME OF THE RARER ELEMENTS

Apart from a study of the reactions of lithium (Section **III, 37**), no reference has been made in the earlier chapters to the characteristic reactions of the so-called "rarer elements." Many of these, *e.g.*, tungsten, molybdenum, titanium, uranium and beryllium, have important industrial applications, and it was felt that a brief account of the analytical chemistry of a number of selected elements might usefully be included in this volume.

The term "rarer elements" as originally employed in the sense of their comparative rare occurrence and limited availability must now, in a number of cases, be regarded as a misnomer. Large quantities of some of these elements are utilised annually, and the range of their application is slowly but surely widening. Two examples may be mentioned: the use of (*a*) molybdenum, tungsten, titanium and beryllium in the steel industry, and (*b*) of titanium and uranium in the paint industry. The interpretation of the term "rarer elements," as applied to the elements described in this Chapter, is perhaps best accepted in the sense of their comparatively rare occurrence in routine qualitative analysis.

No attempt has been made to give more than a short introduction to the subject; to economise space, most of the simple equations have been omitted. The elements have been classified, in so far as is possible, in the simple Groups with which the student is already familiar, and methods of separation have been briefly indicated. Thus thallium and tungsten are in Group I; molybdenum, gold, platinum, selenium, tellurium and vanadium in Group II; and beryllium, titanium, uranium, thorium and cerium in Group III. Vanadium, although not actually precipitated by hydrogen sulphide in acid solution, is placed in Group II because of its similarity with many of the reactions of this Group. Moreover, its presence will be revealed by the blue colour and absence of precipitate produced by hydrogen sulphide in acid solution, although its actual isolation as sulphide is effected by the addition of acid to the ammonium sulphide solution in Group IIIB. The reader is referred to the standard work on the subject, A. A. Noyes and W. C. Bray, *A System of Qualitative Analysis for the Rare Elements* (Macmillan, 1927), wherein a comprehensive account of the methods of separation and identification of most of the known solid elements is given, for more detailed treatment. It is hoped, however, that the subject matter of this chapter will suffice to enable the student to detect the presence of one or two of the compounds of the "rarer elements" in a mixture*.

THALLIUM, Tl

Thallium forms two oxides TlO and Tl_2O_3 from which the thallous and thallic salts respectively are derived. The thallous salts are the more stable and hence of greater interest from the analytical view point. Thallic salts are comparatively unstable and readily hydrolyse in solution: thus, when an aqueous solution of thallic sulphate or nitrate is boiled thallic hydroxide is precipitated. Thallous salts are oxidised to thallic by potassium permanganate, potassium ferricyanide, lead dioxide, bromine, chlorine and *aqua regia* (but not by concentrated nitric acid). The reduction of thallic to thallous compounds is easily effected by stannous chloride, sulphurous acid, ferrous salts, or hydroxylamine.

VII, IA. REACTIONS OF THALLOUS COMPOUNDS

Use a solution of thallous nitrate,‡ $TlNO_3$ or of thallous sulphate, Tl_2SO_4.

1. **Dilute Hydrochloric Acid**: white precipitate of thallous chloride TlCl, sparingly soluble in cold, but more soluble in hot water (compare lead).

2. **Potassium Iodide Solution**: yellow precipitate of thallous iodide TlI, almost insoluble in water; it is also insoluble in cold sodium thiosulphate solution (difference and method of separation from lead).

† The spot-test technique is as follows. Place a drop of the faintly acid test solution on a black spot plate or upon a blackened watch glass. Add a drop of 10 per cent potassium iodide solution and, when a precipitate appears, a drop or two of 2 per cent sodium thiosulphate solution. A yellow precipitate is produced.

Sensitivity: 0·6 μg. Tl. Concentration limit: 1 in 80,000.

The potassium iodide removes mercury as potassium mercuri-iodide $K_2[HgI_4]$, whilst the sodium thiosulphate dissolves lead and silver as complex thiosulphates.

3. **Potassium Chromate Solution**: yellow precipitate of thallous chromate Tl_2CrO_4, insoluble in cold nitric or sulphuric acid.

4. **Hydrogen Sulphide**: no precipitate in the presence of dilute mineral acid. Incomplete precipitation of black thallous sulphide Tl_2S occurs in neutral or acetic acid solution.

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* Such knowledge is required of students preparing for the Associateship of the Institute of Chemistry, the Fellowship of the Institute of Chemistry in Inorganic Chemistry, and for certain University examinations.

‡ Test solutions containing 10 milligrams per c.c. of the reactive anion or cation of the "rarer elements" should be prepared by the student when required (compare Section **A, 3**); a volume of 25–50 c.c. will usually suffice.

5. **Ammonium Sulphide Solution**: black precipitate of thallous sulphide Tl_2S, soluble in mineral acids. The precipitate is oxidised to thallous sulphate Tl_2SO_4 upon exposure to air.

Owing to the slight solubility of thallous chloride, some of the thallium is also precipitated in Group IIIB (compare lead). It is often, however, precipitated with Group II ions.

6. **Sodium Cobaltinitrite Solution**: light-red precipitate of thallous cobaltinitrite $Tl_3[Co(NO_2)_6]$.

7. **Chloroplatinic Acid Solution**: pale-yellow precipitate of thallous chloroplatinate $Tl_2[PtCl_6]$, almost insoluble in water (solubility, 0·06 g. per litre at 15°).

8. **Potassium Ferricyanide Solution**: brown precipitate of thallic hydroxide, $Tl(OH)_3$ or Tl_2O_3,xH_2O, in alkaline solution. A similar result is obtained with sodium hypochlorite or hypobromite solution or with hydrogen peroxide in alkaline solution.

$$Tl_2SO_4 + 4K_3[Fe(CN)_6] + 6KOH = Tl_2O_3 + 4K_4[Fe(CN)_6] + K_2SO_4 + 3H_2O.$$

9. **Ammonium Thiocyanate Solution**: white precipitate of sparingly soluble thallous thiocyanate, TlCNS.

VII, 1B. REACTIONS OF THALLIC COMPOUNDS

Use a solution of thallic chloride $TlCl_3$, prepared by dissolving thallic oxide or thallic hydroxide in moderately concentrated hydrochloric acid.

1. **Sodium Hydroxide or Ammonium Hydroxide Solution**: brown precipitate of thallic hydroxide, insoluble in excess of the reagent (difference from thallous salts), but readily soluble in hydrochloric acid.

2. **Hydrochloric Acid**: no precipitate (difference from thallous salts).

3. **Potassium Chromate Solution**: no precipitate (difference from thallous salts).

4. **Potassium Iodide Solution**: brownish-black precipitate, probably a mixture of thallous iodide and iodine.

5. **Hydrogen Sulphide**: reduced to the thallous state with the precipitation of sulphur. If the acid is neutralised, thallous sulphide Tl_2S precipitates.

Dry Test.

All thallium salts impart an intense green colouration to the Bunsen flame. This is best identified (and distinguished from barium) with the aid of the spectroscope.

Separation.—The element may be precipitated as TlCl in Group I, separated from AgCl and Hg_2Cl_2 by solution in boiling water, and from $PbCl_2$ by means of dilute H_2SO_4; the thallium can then be precipitated as TlI by the addition of KI solution. It may also be separated from lead by precipitation as the iodide and treatment with $Na_2S_2O_3$ solution, in which PbI_2 alone is soluble. Useful confirmatory tests are reaction *6* (Section **VII, 1A**) and the flame test.

Any thallium not precipitated in Group I as TlCl, will ultimately be found in the precipitate of Group IIIB. It is best to dissolve the Group IIIB precipitate in dilute nitric acid, boil to expel H_2S, add a few drops of sulphurous acid, and boil to expel excess of SO_2. The resultant solution is then poured into excess of sodium carbonate solution when the carbonates of cobalt, nickel, manganese and zinc are precipitated. The thallium remains in solution as thallous carbonate and can be precipitated as thallous sulphide Tl_2S by the addition of ammonium sulphide solution.

TUNGSTEN, W

Tungsten forms an unstable dioxide WO_2, and a stable, yellow acidic oxide WO_3. The latter oxide is almost insoluble in water and in dilute acids, but is soluble in solutions of (best in fused) caustic alkalis forming tungstates. The latter are the most important compounds of tungsten.

Tungstates form complex acids with phosphoric, boric and silicic acids; tungstic acid cannot therefore be precipitated from these compounds by hydrochloric acid. The complexes may usually be decomposed by heating with concentrated sulphuric acid, tungstic acid being liberated.

VII, 2. REACTIONS OF TUNGSTATES

Use a solution of sodium tungstate, $Na_2WO_4,12H_2O$.

1. **Dilute Hydrochloric Acid**: white precipitate of hydrated tungstic acid H_2WO_4,H_2O in the cold; upon boiling the mixture, this is converted into yellow tungstic acid H_2WO_4, insoluble in dilute acids. Similar results are obtained with dilute nitric and sulphuric acids, but not with phosphoric acid. The ppt. is soluble in dilute ammonia solution.

2. **Phosphoric Acid**: white precipitate of phosphotungstic acid $H_3[PO_4(W_{12}O_{36})],5H_2O$, soluble in excess of the reagent.

3. **Hydrogen Sulphide**: no precipitate in acid solution.

4. **Ammonium Sulphide Solution**: no precipitate, but if the solution is afterwards acidified with dilute hydrochloric acid, a brown precipitate of tungsten trisulphide WS_3 is produced. The precipitate dissolves in ammonium sulphide solution forming a thiotungstate $(NH_4)_2[WS_4]$.

5. **Zinc and Hydrochloric Acid.**—If a solution of a tungstate is treated with hydrochloric acid and then a little zinc added, a blue colouration or precipitate is produced; this is probably due to W_2O_5 or to WCl_5.

6. **Stannous Chloride Solution**: yellow precipitate, which becomes blue upon warming with concentrated hydrochloric acid.

† The spot-test technique is as follows. Mix 1–2 drops of the test solution with 3–5 drops of the stannous chloride reagent on a spot plate. A blue precipitate or colouration appears. This is probably due to a lower tungsten oxide.

Sensitivity: 5μg. W. Concentration limit: 1 in 10,000.

Molybdenum salts interfere and should be absent.

The **reagent** consists of a 25 per cent solution of stannous chloride in concentrated hydrochloric acid.

7. **Ferrous Sulphate Solution**: brown precipitate, which is not turned blue by mineral acids (difference from molybdates).

8. **Silver Nitrate Solution**: pale yellow precipitate of silver tungstate, soluble in ammonia solution, decomposed by nitric acid with the formation of white hydrated tungstic acid.

Dry Test

Microcosmic salt bead: oxidising flame—colourless or pale-yellow; reducing flame—blue, changing to blood-red upon the addition of a little ferrous sulphate.

Separation.—Tungsten is precipitated in Group I and is associated with Ag in the ammoniacal filtrate of the group separation. The filtrate is almost neutralised with dilute HCl (any precipitate formed being kept in solution by the addition of ammonia solution), and the silver precipitated as AgI by the addition of KI solution. The filtrate is concentrated, acidified with dilute HCl, and tests *5* or *6* applied.

The following table contains a scheme for the identification of thallous thallium and tungsten (as tungstate) in the presence of lead, mercurous mercury and silver.

VII, 8. Table XLIII. Analysis of Group I (Silver Group) in the presence of Tl and W*

<table>
<tr><td colspan="5">The precipitate may contain $PbCl_2$, AgCl, Hg_2Cl_2, TlCl and tungstic acid. Wash the precipitate on the filter with dilute HCl, then 2–3 times with <i>small</i> amounts of <i>cold</i> water, and reject the washings. Transfer the ppt. ‡ to a boiling tube or to a small beaker, and boil with 15–20 c.c. of water. Filter hot.</td></tr>
<tr><td colspan="3">Residue. May contain Hg_2Cl_2, AgCl and tungstic acid. Wash the ppt. several times with hot water until the washings give no ppt. with K_2CrO_4 solution ; this ensures the complete removal of the Pb and Tl.
Pour 10–15 c.c. of warm NH_4OH solution (1:1) over the precipitate and collect the filtrate.</td><td colspan="2">Filtrate. May contain $PbCl_2$ and TlCl. Evaporate to fuming with H_2SO_4, cool, dilute and filter.</td></tr>
<tr><td rowspan="2">Residue. If black, consists of $Hg(NH_2)Cl + Hg$.
Hg(ous) present.</td><td colspan="2">Filtrate. May contain $[Ag(NH_3)_2]Cl$ and ammonium tungstate. Nearly neutralise with dilute HCl and add just enough dilute NH_4OH to redissolve any ppt. which forms. Add KI solution and filter.</td><td rowspan="2">Residue. If white— consists of $PbSO_4$. This is soluble in ammonium acetate solution ; K_2CrO_4 solution precipitates yellow $PbCrO_4$, soluble in NaOH solution.
Pb present.</td><td rowspan="2">Filtrate. May contain Tl_2SO_4. Just neutralise with NH_4OH solution (1 : 1), and add KI solution. Yellow ppt. (TlI), insoluble in cold $Na_2S_2O_3$ solution.
Tl present.
Confirm by flame test: intense green flame.</td></tr>
<tr><td>Residue Pale-yellow (AgI)
Ag present.</td><td>Filtrate. May contain a tungstate. Evaporate to a small volume, acidify with dilute HCl, add 3 c.c. of <i>N</i>-$SnCl_2$, boil, add 3 c.c. of conc. HCl, and heat again to boiling.
Blue ppt. or colouration.
W present.</td></tr>
</table>

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* Compare Table XXVII, Section **V, 9.**

‡ A gelatinous precipitate may also be hydrated silica, which is partially precipitated here from silicates decomposable by acids.

MOLYBDENUM, Mo

Molybdenum forms three basic oxides MoO, Mo_2O_3 and MoO_2, and one acidic oxide MoO_3. The last-named is the most important; it is sparingly soluble in water, but dissolves readily in solutions of alkalis forming molybdates.

VII, 4. REACTIONS OF MOLYBDATES

Use a solution of ammonium molybdate $(NH_4)_6Mo_7O_{24},4H_2O$.

1. **Dilute Hydrochloric Acid**: white or yellow precipitate of molybdic acid H_2MoO_4, soluble in excess of mineral acid.

2. **Hydrogen Sulphide.**—With a small quantity of the gas and an acidified molybdate solution, a blue colouration is produced; further passage of hydrogen sulphide yields a brown precipitate of the trisulphide MoS_3, soluble in ammonium sulphide solution to a brown solution containing a thiomolybdate $(NH_4)_2[MoS_4]$, from which MoS_3 is reprecipitated by the addition of acids. The precipitation in acid solution is incomplete in the cold; more extensive precipitation is obtained by the prolonged passage of the gas into the boiling solution. Precipitation is quantitative with excess of hydrogen sulphide at 0° in the presence of formic acid.

3. **Reducing Agents,** *e.g.*, zinc, stannous chloride solution: colour a molybdate solution acidified with dilute hydrochloric acid blue (probably due to $MoCl_3$), then green and finally brown.

4. **Ammonium Thiocyanate Solution**: yellow colouration in solution acidified with dilute hydrochloric acid, becoming blood red upon the addition of zinc or of stannous chloride on account of the formation of ammonium molybdo-thiocyanate $(NH_4)_3[Mo(CNS)_6]$; the latter is soluble in ether. The red colouration is produced in the presence of phosphoric acid (difference from iron).

† The spot-test technique is as follows. Place a drop of the test solution and a drop of potassium or ammonium thiocyanate solution on quantitative filter paper or drop-reaction paper which has been soaked in 1:1 hydrochloric acid. Add a drop of stannous chloride solution. A red spot is obtained.

Sensitivity: 0·1 μg. Mo. Concentration limit: 1 in 500,000.

If iron is present, a red spot will appear initially but this disappears upon the addition of the stannous chloride (or of sodium thiosulphate) solution. Tungstates interfere since they give a blue spot of a lower tungsten oxide; however, this is prevented by soaking the paper in hydrochloric acid whereby insoluble tungstic acid is formed and the molybdenum diffuses through the capillaries of the paper to the edge of the drop and is identified there.

5. **Sodium Phosphate Solution**: yellow, crystalline precipitate of ammonium phosphomolybdate in the presence of excess of nitric acid (compare Phosphates, Section **IV, 28**, reaction *4*).

6. **Potassium Ferrocyanide Solution**: brown precipitate of molybdenum ferrocyanide $Mo_2[Fe(CN)_6]_2$, insoluble in dilute mineral acids, but readily soluble in solutions of caustic alkalis and ammonium hydroxide (difference from uranyl and cupric ferrocyanides).

7. α-**Benzoin Oxime Reagent** (or **"Cupron" Reagent**).—The molybdate solution is strongly acidified with dilute sulphuric acid and 0·5 c.c. of the reagent added. A white precipitate is produced.

8. **Potassium Xanthate** (or **Potassium Ethyl Xanthogenate**) **Test** $\{SC(SK)OC_2H_5\}$.—When a molybdate solution is treated with a little solid potassium xanthate and then acidified with dilute hydrochloric acid, a red-purple colouration is produced. With large amounts of molybdenum, the compound separates as dark oily drops which are readily soluble in organic solvents such as benzene, chloroform and carbon disulphide. The reaction product has been given the formula $MoO_2[SC(SH)(OC_2H_5)]_2$. The test is said to be specific for molybdates, although copper, cobalt, nickel, iron, chromium and uranium under exceptional conditions interfere. Large quantities of oxalates, tartrates and citrates decrease the sensitivity of the test.

† The spot-test technique, for which the reaction is particularly well adapted, is as follows. Place a drop of the nearly neutral or faintly acid test solution on a spot plate, introduce a minute crystal of potassium xanthate, followed by 2 drops of 2*N*-hydrochloric acid. An intense red-violet colouration is obtained.

Sensitivity: 0·04 μg. Mo. Concentration limit: 1 in 250,000.

† *9.* **Phenylhydrazine Reagent** ($C_6H_5.NHNH_2$).—A red colouration or precipitate is produced when molybdates and an acid solution of phenylhydrazine react. The latter is oxidised by the molybdate to a diazonium salt, which then couples with the excess of base and the molybdate to yield a coloured compound.

Mix a drop of the test solution and a drop of the reagent on a spot plate. A red colouration appears.

Sensitivity: 0·3 μg. Mo. Concentration limit: 1 in 150,000.

Alternatively, place a drop of the reagent on drop reaction paper and immediately add a drop of the test solution. A red ring forms round the spot.

Sensitivity: 0·1 μg. Mo. Concentration limit: 1 in 300,000.

The **reagent** consists of a solution of 1 part of phenylhydrazine dissolved in 2 parts of glacial acetic acid.

Dry Tests

(i) *Microcosmic salt bead*: oxidising flame—yellow to green while hot and colourless when cold; reducing flame—brown when hot, green when cold.

(ii) Upon evaporation with concentrated sulphuric acid in a porcelain dish or crucible, a blue mass (containing "molybdenum blue") is obtained.

Separation.—Molybdenum appears along with As, Sb, Sn, Au and Pt in the ordinary process of analysis. Upon acidification of the yellow ammonium sulphide solution extract and boiling with concentrated HCl, MoS_3 appears with the As_2S_3. The mixture of MoS_3 and As_2S_3 is dissolved in HNO_3, the As removed with magnesia mixture, and the Mo detected in the filtrate by test *4* or *8* or the dry test (ii).

See also Table XLIV in Section **VII, 9.**

GOLD, Au

Gold is a very stable metal. It is unattacked by mineral acids, but dissolves readily in aqua regia :

$$2Au + 2HNO_3 + 8HCl = 2H[AuCl_4] + 2NO + 4H_2O.$$

The metal is also soluble *inter alia* in chlorine and bromine water forming respectively $AuCl_3$ and $AuBr_3$; these combine with potassium chloride and potassium bromide to produce the crystalline aurichloride $K[AuCl_4]$ and auribromide $K[AuBr_4]$ respectively. The commercial metal is usually alloyed with copper and/or silver.

Two oxides Au_2O and Au_2O_3 are known ; these correspond to the aurous and auric salts respectively. The latter are the more stable and exhibit a marked tendency to form complex salts of the type $R[AuX_4]$.

VII, 5. REACTIONS OF AURIC COMPOUNDS

Use a solution of gold chloride (hydrogen aurichloride), $H[AuCl_4],3H_2O$.

1. **Hydrogen Sulphide** : black precipitate of aurous sulphide Au_2S in the cold, insoluble in dilute acids, but soluble in yellow ammonium sulphide solution, from which it is reprecipitated by dilute hydrochloric acid. A brown precipitate of metallic gold, together with sulphur, is obtained upon precipitation of a hot solution ; this is also dissolved by yellow ammonium sulphide solution.

$$2H[AuCl_4] + 3H_2S = Au_2S + 2S + 8HCl.$$

2. **Ammonium Hydroxide Solution** : yellow precipitate of " fulminating gold," $Au(NH)Cl + Au(NH)NH_2$. The dry substance explodes upon heating or upon percussion.

3. **Oxalic Acid Solution.**—Gold is precipitated as a fine brown powder (or sometimes as a mirror) from cold neutral solutions (difference from platinum and other Group II metals). Under suitable conditions, the gold is obtained in the colloidal state as a red, violet or blue solution.

$$2H[AuCl_4] + 3H_2.C_2O_4 = 2Au + 8HCl + 6CO_2.$$

Similar results are obtained with ferrous sulphate solution. Reduction also occurs with hydroxylamine and hydrazine salts.

4. **Stannous Chloride Solution**: purple precipitate, "purple of Cassius," consisting of an adsorption compound of stannous hydroxide $Sn(OH)_2$ and colloidal gold, in neutral or weakly acid solution. In extremely dilute solutions, only a purple colouration is produced. If the solution is strongly acid with hydrochloric acid, a dark brown precipitate of pure gold is formed.

$$2H[AuCl_4] + 3SnCl_2 = 2Au + 3SnCl_4 + 2HCl.$$

5. **Hydrogen Peroxide**: the finely divided metal is precipitated in the presence of sodium hydroxide solution (distinction from platinum). The precipitated metal appears brownish-black by reflected light and bluish-green by transmitted light.

$$2H[AuCl_4] + 3H_2O_2 + 8NaOH = 2Au + 8NaCl + 3O_2 + 8H_2O.$$

6. **Sodium Hydroxide Solution**: reddish-brown precipitate of auric hydroxide $Au(OH)_3$ from *concentrated* solutions. The precipitate has amphoteric properties; it dissolves in excess of alkali forming aurates containing the $[AuO_2]^{--}$ ion.

† *7.* **para-Dimethylamino-benzylidene-rhodanine Reagent***: red-violet precipitate in neutral or faintly acid solution. Silver, mercury and palladium salts give coloured compounds with the reagent and must therefore be absent.

Moisten a piece of drop-reaction paper with the reagent and dry it. Place a drop of the neutral or weakly acid test solution, upon it. A violet spot or ring is obtained.

Sensitivity: 0·1 μg. Au. Concentration limit: 1 in 500,000.

The **reagent** consists of a 0·03 per cent solution of *p*-dimethylamino-benzylidene-rhodanine in acetone.

Dry Test

All gold compounds when heated upon charcoal with sodium carbonate yield yellow, malleable, metallic particles, which are insoluble in nitric acid, but soluble in aqua regia. The aqua regia solution should be evaporated to dryness, dissolved in water, and tests *1*, *3* or *4* applied.

Separation.—Gold is usually detected and determined by dry methods. In the wet way, it is precipitated by H_2S in Group II, dissolved by yellow ammonium sulphide solution, and reprecipitated from the latter by concentrated HCl along with As_2S_3 and MoS_3. Separation from As_2S_3 and MoS_3 is effected by concentrated HNO_3, in which the gold precipitate is insoluble. The gold may then be dissolved in aqua regia, and identified by tests *1*, *3* or *4*.

See also Table XLIV in Section **VII, 9.**

PLATINUM, Pt

Platinum, like gold, is unattacked by mineral acids; it dissolves in aqua regia to form a yellowish-orange solution of chloroplatinic acid $H_2[PtCl_6]$:

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* For formula, see under Silver, Section **III, 4**, reaction 7.

$$3Pt + 4HNO_3 + 18HCl = 3H_2[PtCl_6] + 4NO + 8H_2O.$$

This acid and its salts are the most commonly occurring platinum compounds.

VII, 6. REACTIONS OF CHLOROPLATINATES

Use a solution of chloroplatinic acid, $H_2[PtCl_6],6H_2O$*.

1. **Hydrogen Sulphide** : black (or dark brown) precipitate of the disulphide PtS_2, slowly formed in the cold, but rapidly on warming. The precipitate is insoluble in concentrated acids, but dissolves in aqua regia and also in yellow ammonium sulphide solution ; it is reprecipitated from the last-named solution of thio salt by dilute acids.

$$H_2[PtCl_6] + 2H_2S = PtS_2 + 6HCl.$$

2. **Potassium Chloride Solution** : yellow precipitate of potassium chloroplatinate $K_2[PtCl_6]$ from concentrated solutions (difference from gold). A similar result is obtained with ammonium chloride solution.

3. **Oxalic Acid Solution** : no precipitate of platinum (difference from gold). Hydrogen peroxide and sodium hydroxide solution likewise do not precipitate metallic platinum.

4. **Formic Acid** : black powder of metallic platinum from neutral boiling solutions.

$$Na_2[PtCl_6] + 2HCOOH = Pt + 2NaCl + 4HCl + 2CO_2.$$

5. **Zinc, Cadmium, Magnesium or Aluminium** : all these metals precipitate finely divided platinum.

$$H_2[PtCl_6] + 3Zn = 2Pt + 3ZnCl_2 + H_2.$$

6. **Hydrazine Hydrochloride** : ready reduction in ammoniacal solution to metallic platinum, some of which is deposited as a mirror upon the sides of the tube.

$$(NH_4)_2[PtCl_6] + N_2H_4,2HCl + 6NH_4OH \\ = 8NH_4Cl + 6H_2O + N_2 + Pt.$$

7. **Silver Nitrate Solution** : yellow precipitate of silver chloroplatinate $Ag_2[PtCl_6]$, sparingly soluble in ammonia solution but soluble in solutions of alkali cyanides and of alkali thiosulphates.

8. **Potassium Iodide Solution** : intense brownish-red or red colouration, due to $[PtI_6]^{--}$ ions. With excess of the reagent $K_2[PtI_6]$ may be precipitated as an unstable brown solid. On warming, black PtI_4 may be precipitated.

9. **Stannous Chloride Solution** : red or yellow colouration, due to colloidal platinum, soluble in ethyl acetate or in ether.

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† To employ this reaction as a spot test in the presence of other noble metals (gold, palladium, etc.), the platinum is fixed as thallous chloro-

* Commonly called "platinic chloride."

platinate $Tl_2[PtCl_6]$, which is stable to ammonia solution ; upon washing the precipitate with ammonia solution, the thallium complexes with gold, palladium, etc., pass into solution.

Place a drop of saturated thallous nitrate solution upon drop-reaction paper, add a drop of the test solution and then another drop of the thallous nitrate solution. Wash the precipitate with ammonia solution, and add a drop of strongly acid stannous chloride solution. A yellow or orange spot remains.

Sensitivity : 0·025 μg. Pt. (in 0·002 c.c.). Concentration limit : 1 in 80,000.

† *10.* **Nickel Acetate-Sodium Hypophosphite Test.** Sodium hypophosphite very slowly reduces aqueous solutions of nickel salts to metallic nickel (and some nickel phosphide). The reaction is considerably accelerated by small amounts of platinum (and other platinum metals including palladium).

Place into two perfectly clean test-tubes both 10 c.c. of 1 per cent nickel acetate solution and 1 c.c. of saturated sodium hypophosphite solution. Introduce 1 c.c. of the neutral or faintly acid test solution into one tube and 1 c.c. of water (blank test) into the other. Stand both tubes in a beaker of boiling water. Hydrogen is soon evolved and in 2–30 minutes, according to the noble metal content of the solution, nickel is deposited from the platinum-containing solution, partly as a black powder and partly as a metallic mirror. The blank test remains green.

Sensitivity : 1·5 μg. Pt (in 1 c.c.). Concentration limit : 1 in 6,600,000.

Dry Test

All platinum compounds when fused with sodium carbonate upon charcoal are reduced to the grey, spongy metal (distinction from gold). The residue is insoluble in concentrated mineral acids, but dissolves in aqua regia. The solution is evaporated almost to dryness, dissolved in water, and tests *1*, *2*, *5*, *9* or *10* applied.

Separation.—Platinum is precipitated in Group II as PtS_2. The Group IIB metals are extracted with yellow ammonium sulphide solution and reprecipitated with HCl. The sulphides of As, Sb, Sn, Au, Pt and Mo are dissolved in aqua regia, the excess of acid evaporated, and NH_4Cl solution added. A yellow precipitate of $(NH_4)_2[PtCl_6]$ indicates the presence of Pt. The filtrate is treated with $FeSO_4$ solution ; Au is precipitated and is removed. The filtrate is again treated with H_2S to reprecipitate As, Sb, Sn and Mo as sulphides, which are filtered off. These sulphides are then separated as described under Molybdates (Section **VII, 4**).

See also Table XLIV in Section **VII, 9.**

SELENIUM, Se

Selenium resembles sulphur in many of its properties. It is converted by nitric acid or by aqua regia into selenium dioxide SeO_2 (or selenious acid H_2SeO_3). In analytical work the element is most frequently encountered in the form of selenites R_2SeO_3 and as the less stable selenates R_2SeO_4.

VII, 7A. REACTIONS OF SELENITES

Use a solution of selenious acid, H_2SeO_3*.

1. **Hydrogen Sulphide** : yellow precipitate, consisting of a mixture of selenium and sulphur, in the cold, becoming red on heating. The precipitate is readily soluble in yellow ammonium sulphide solution.

$$H_2SeO_3 + 2H_2S = Se + 2S + 3H_2O.$$

2. **Reducing Agents** (sulphur dioxide, solutions of stannous chloride, ferrous sulphate, hydroxylamine hydrochloride, hydrazine hydrochloride or hydriodic acid (KI + HCl), zinc or iron) : red precipitate of selenium in hydrochloric acid solution. The precipitate frequently turns greyish-black on warming.

3. **Copper Sulphate Solution** : bluish-green, crystalline precipitate of copper selenite $CuSeO_3$ in neutral solution (difference from selenate).

4. **Barium Chloride Solution** : white precipitate of barium selenite $BaSeO_3$ in neutral solution, soluble in dilute mineral acids.

† *5.* **Thiourea Test** $\{CS(NH_2)_2\}$.—Solid or dissolved thiourea precipitates selenium as a red powder from cold dilute solutions of selenites. Tellurium and bismuth give yellow precipitates, whilst large amounts of nitrites and of copper interfere.

Place a little powdered thiourea on quantitative filter paper and moisten it with a drop of the test solution. Orange-red selenium separates out.

Sensitivity : 0·1 μg. Se. Concentration limit : 1 in 500,000.

† *6.* **Hydriodic Acid Test.**—Selenites are reduced by hydriodic acid (or by potassium iodide and hydrochloric acid) :

$$H_2SeO_3 + 4HI = Se + 2I_2 + 3H_2O.$$

The iodine is removed by adding a thiosulphate, and the selenium remains as a reddish-brown powder. Tellurites react under these conditions forming the complex anion $[TeI_6]^{--}$, which also has a reddish-brown colour ; it is however decomposed and decolourised by a thiosulphate, thus permitting the detection of selenium in the presence of not too large an excess of tellurium.

Place a drop of concentrated hydriodic acid (or a drop each of concentrated potassium iodide solution and of concentrated hydrochloric acid) upon drop-reaction paper and introduce a drop of the acid test solution into the middle of the original drop. A brownish-black spot appears. Add a drop of 5 per cent sodium thiosulphate solution to the spot ; a reddish-brown stain of elementary selenium remains.

Sensitivity : 1 μg. Se (in 0·025 c.c.). Concentration limit : 1 in 25,000.

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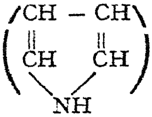
* Also produced by dissolving selenium dioxide SeO_2 in water.

† 7. **Pyrrole Reagent** .—Selenious acid oxidises pyrrole to a blue dyestuff of unknown composition (" pyrrole blue "). Iron salts accelerate the reaction when it is carried out in phosphoric acid solution. Selenic, tellurous and telluric acids do not react under the conditions given below: the test therefore provides a method of distinguishing selenites and selenates.

Place a drop of 5 per cent ferric chloride solution and 7 drops of syrupy phosphoric acid (sp. gr. 1·75) on a spot plate containing 1 drop of the test solution and stir well. Add a drop of the pyrrole reagent and stir again. A greenish-blue colouration is obtained.

Sensitivity: 0·5 μg. Se. Concentration limit: 1 in 100,000.

The **reagent** consists of a 1 per cent solution of pyrrole in aldehyde-free ethyl alcohol.

VII, 7B. REACTIONS OF SELENATES

Use a solution of potassium selenate, K_2SeO_4.

1. **Hydrogen Sulphide**: no precipitation occurs. If the solution is boiled with concentrated hydrochloric acid, the selenic acid is reduced to selenious acid; hydrogen sulphide then precipitates a mixture of selenium and sulphur.

$$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O.$$

2. **Sulphur Dioxide**: no reducing action.

3. **Copper Sulphate Solution**: no precipitate (difference from selenite).

4. **Barium Chloride Solution**: white precipitate of barium selenate $BaSeO_4$, insoluble in dilute mineral acids. The precipitate dissolves when boiled with concentrated hydrochloric acid, and chlorine is evolved (distinction and separation from sulphate).

$$BaSeO_4 + 4HCl = H_2SeO_3 + BaCl_2 + Cl_2 + H_2O.$$

Dry Tests

(i) All selenium compounds when mixed with sodium carbonate and heated upon charcoal emit the odour of rotten horseradish. A foul odour, due to hydrogen selenide H_2Se, is obtained upon moistening the residue with a few drops of dilute hydrochloric acid. A black stain (due to Ag_2Se) is produced when the moistened residue is placed in contact with a silver coin.

(ii) Elementary selenium dissolves in concentrated sulphuric acid to yield a green solution, due to the presence of the compound $SSeO_3$. Upon dilution with water, red selenium is precipitated.

Separation.—See under tellurium (Section **VII, 8**).

TELLURIUM, Te

Tellurium is less widely distributed in nature than selenium ; both elements belong to Group VI of the periodic system. When fused with potassium cyanide, it is converted into potassium telluride K_2Te, which dissolves in water to yield a red solution. If air is passed through the solution, the tellurium is precipitated as a black powder (difference and method of separation from selenium). Selenium under similar conditions yields the stable potassium selenocyanide KCNSe ; the selenium may be precipitated by the addition of dilute hydrochloric acid to its aqueous solution.

$$2KCN + Te = K_2Te + (CN)_2;$$
$$2K_2Te + 2H_2O + O_2 = 2Te + 4KOH.$$
$$KCN + Se = KCNSe;$$
$$KCNSe + HCl = Se + KCl + HCN.$$

Tellurium is converted into the dioxide TeO_2 by nitric acid. Like sulphur and selenium, it forms two series of salts, the tellurites R_2TeO_3 and the tellurates R_2TeO_4.

VII, 8A. REACTIONS OF TELLURITES

Use a solution of potassium tellurite, K_2TeO_3.

1. **Hydrogen Sulphide** : brown precipitate of the disulphide TeS_2 from acid solutions. The sulphide decomposes easily into tellurium and sulphur, and is readily soluble in ammonium sulphide solution.

2. **Sulphur Dioxide** : complete precipitation of tellurium from dilute hydrochloric acid solutions as a black powder. In the presence of much hydrochloric acid, no precipitate is formed (difference and method of separation from selenium).

3. **Ferrous Sulphate Solution** : no precipitation of tellurium (difference from selenium). A similar result is obtained with hydriodic acid (KI + HCl).

4. **Stannous Chloride or Hydrazine Hydrochloride Solution or Zinc** : black tellurium is precipitated.

5. **Dilute Hydrochloric Acid** : white precipitate of tellurous acid H_2TeO_3.

6. **Barium Chloride Solution** : white precipitate of barium tellurite $BaTeO_3$.

7. **Potassium Iodide Solution** : black precipitate of TeI_4 in faintly acid solution, dissolving in excess of the reagent to form the red potassium telluri-iodide $K_2[TeI_6]$ (difference from selenites).

† *8.* **Hypophosphorous Acid Test.**—Both tellurites and tellurates are reduced to tellurium upon evaporation with hypophosphorous acid :

$$H_2PO_2^- + TeO_3^{--} = PO_4^{---} + Te + H_2O;$$
$$3H_2PO_2^- + 2TeO_4^{--} = 3PO_4^{--} + 2Te + 2H^+ + 2H_2O$$

Selenites are likewise reduced to selenium. If, however, the solution of the selenite in concentrated sulphuric acid is treated with sodium sulphite, selenium separates but the tellurite is unaffected ; the latter can be detected in the solution after eliminating the sulphur dioxide. Salts of silver, copper, gold and platinum must be absent for they are reduced to the metal by the reagent.

Mix a drop of the test solution in mineral acid and a drop of 50 per cent hypophosphorous acid in a porcelain micro-crucible, and evaporate almost to a dryness. Black grains or a grey stain of tellurium are obtained.

Sensitivity : 0·1 μg. tellurous acid ; concentration limit : 1 in 500,000; 0·5 μg. telluric acid ; concentration limit : 1 in 100,000.

VII, 8B. REACTIONS OF TELLURATES

Use a solution of potassium tellurate, K_2TeO_4.

1. **Hydrogen Sulphide** : no precipitate in hydrochloric acid solution in the cold. In hot acid solution, the tellurate is first reduced to tellurite, and precipitation of the tellurium then occurs (compare Section **VII, 8A**). Other reducing agents give similar results.

$$K_2TeO_4 + 2HCl = K_2TeO_3 + H_2O + Cl_2.$$

2. **Hydrochloric Acid** : no precipitate in the cold. Upon boiling the solution, chlorine is evolved ; tellurous acid H_2TeO_3 is thrown down upon dilution (distinction from selenium).

3. **Barium Chloride Solution** : white precipitate of barium tellurate $BaTeO_4$ from concentrated solutions.

Dry Tests

(i) Fusion of any tellurium compound with sodium carbonate upon charcoal results in the formation of sodium telluride Na_2Te, which produces a black stain (due to Ag_2Te) when placed in contact with a moist silver coin.

(ii) Elementary tellurium dissolves in concentrated sulphuric acid to yield a red solution, due to the presence of $STeO_3$. Upon dilution with water, grey tellurium is precipitated.

Separation.—Selenium and tellurium are precipitated in Group II as the yellow Se–S mixture and brown Te–S mixture respectively. Both dissolve in ammonium sulphide solution and are precipitated with As_2S_3 upon the addition of concentrated HCl. They are best identified by the H_2SO_4 tests.

The following table contains a scheme for the separation of the Group II elements in the presence of Mo, Au, Pt, Se and Te.

VII, 9. Table XLIV.—Analysis of Group II (Copper and Arsenic Groups) in the Presence of Mo, Au, Pt, Se and Te*

Hydrogen sulphide in acid solution precipitates Mo‡, Au, Pt, Se and Te in addition to the "common" elements of Group II. Extraction of the group precipitate with yellow ammonium sulphide solution brings the greater part of the "rarer" elements into Group IIB (arsenic group) but not completely, for appreciable quantities of Mo, Au and Pt remain in the Group IIA (copper group) precipitate. The latter three elements are therefore also tested for in Group IIA.

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* Compare corresponding tables in Sections **V, 10 – V, 12.**

‡ For the almost complete precipitation of Mo in Group II, it has been recommended that the solution be first saturated in the cold with hydrogen sulphide, then transferred to a pressure bottle and heated on a water bath.

Transfer the Group II precipitate, which has been well washed with H_2S water, to a porcelain dish, add about 10 c.c. of yellow ammonium sulphide solution, heat to 50°–60°C, and maintain at this temperature for 3–4 minutes with constant stirring. Filter. Wash the precipitate with dilute ammonium sulphide solution.

Residue. May contain HgS, PbS, Bi_2S_3, CuS, CdS together with Au, Pt, Mo (trace), Sn (trace) as sulphides. **Group IIA present.**	**Filtrate.** May contain solutions of the thio-salts of As, Sb and Sn together with Mo, Au, Pt, Se and Te. Just acidify by adding concentrated HCl drop by drop (test with litmus paper) and warm gently. A coloured precipitate indicates **Group IIB present.**

Proceed to the analysis of Groups IIA and IIB as detailed below.

Table XLIVA.—Analysis of Group IIA (Copper Group)

The ppt may contain HgS, PbS, Bi_2S_3, CuS and CdS together with the sulphides of Au, Pt, Sn (trace) and Mo (trace). Transfer to a beaker or dish, add 15–20 c.c. of dilute HNO_3, boil for 2–5 minutes, and filter.

Residue. May contain sulphides of Hg, Pt and Au. Boil with a little bromine water, and filter, if necessary from traces of SnO_2 and $PbSO_4$ which may separate here. Add KCl solution and HCl, and concentrate the solution. Filter.	**Filtrate.** May contain nitrates of Pb, Bi, Cu and Cd. Examine by Table XXIX in Section **V, 11.**

Residue. Yellow and crystalline $K_2[PtCl_6]$. **Pt present.**	**Filtrate.** May contain $AuCl_3$ and $HgCl_2$. Boil to remove excess of acid, render alkaline with NaOH solution, and boil with excess of oxalic acid. Filter.

Residue. Brownish-black or purplish-black **Au present.**	**Filtrate.** May contain $HgCl_2$. Add a few drops of $SnCl_2$ solution. White or grey ppt.* **Hg present.**

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* Alternatively, the ethylenediamine test (Section **III, 5,** reaction 7) may be applied to the neutral or slightly ammoniacal solution.

Table XLIVB.—Analysis of Group IIB (Arsenic Group)

<table>
<tr><td colspan="7">Transfer the ppt. to a small conical flask, add 10 c.c. of concentrated HCl, and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2–3 c.c. of water, and filter.</td></tr>
<tr><td colspan="6">Residue. May contain As, Au, Pt, Mo, Se and Te as sulphides. Dissolve in concentrated HCl + a little solid $KClO_3$; concentrate the solution to the crystallisation point (use a water bath to reduce loss of Se to a minimum). Filter.</td><td rowspan="6">Filtrate. May ontain Sb and as chlorides complex hloro-acids. xamine by able XXX in ection V, 12.</td></tr>
<tr><td rowspan="5">Residue. Yellow $K_2[PtCl_6]$. Pt present. Confirm by dissolving in little hot water and adding KI solution. Red or brownish-red colouration.</td><td colspan="5">Filtrate. May contain As, Au, Mo, Se, and Te as chlorides or acids. Render alkaline with ammonia solution, add magnesia mixture, allow to stand for 5 minutes with frequent stirring or shaking. Filter.</td></tr>
<tr><td rowspan="4">Residue. White crystalline $Mg(NH_4)AsO_4,6H_2O$ As present.</td><td colspan="4">Filtrate. May contain Au, Mo, Se and Te as chlorides or acids. Concentrate to remove ammonia, boil with several c.c. of saturated oxalic acid solution, dilute, boil, and filter. Extract ppt. with HCl to remove coprecipitated tellurous acid.</td></tr>
<tr><td rowspan="3">Residue. Brownish-black or purplish-black. Au present.</td><td colspan="3">Filtrate. Concentrate with strong HCl on a water bath and, after removing the precipitated KCl, treat with a slight excess of solid Na_2SO_3. Filter.</td></tr>
<tr><td rowspan="2">Residue. Red. Se present.</td><td colspan="2">Filtrate. Dilute with an equal volume of water, and add successively a little KI solution and excess of solid Na_2SO_3 whereby the $K_2[TeI_6]$ is reduced to Te. Filter.</td></tr>
<tr><td>Residue. Black. Te present.</td><td>Filtrate. Boil with HCl to remove excess of SO_2 and treat successively with 10 per cent NH_4CNS solution and a little $SnCl_2$ solution. Red colouration soluble in ether. Mo present. Confirm by potassium xanthate test.</td></tr>
</table>

VANADIUM, V

The most important compounds of vanadium are derived from the oxides V_2O_4 and V_2O_5, both of which exhibit acidic properties, but the latter to the greater degree. Vanadium pentoxide, the anhydride of vanadic acid, is only slightly soluble in water, but dissolves readily in concentrated solutions of caustic alkalis, forming vanadates. Vanadic acid, like phosphoric acid, exists in the form of meta-, pyro- and ortho- compounds (HVO_3, $H_4V_2O_7$ and H_3VO_4 respectively). Unlike the salts of phosphoric acid, the meta-vanadates are the most stable and the ortho-vanadates the least stable. A solution of an ortho-vanadate passes on boiling into the meta-vanadate, the pyro-salt being intermediately formed.

VII, 10. REACTIONS OF VANADATES

Use a solution of ammonium (meta-) vanadate, NH_4VO_3, or the more soluble sodium meta-vanadate, $NaVO_3$.

1. **Hydrogen Sulphide.**—No precipitate is produced in acid solution, but a blue solution (due to the production of a quadrivalent vanadium compound) is formed and sulphur separates. Other reducing agents, such as sulphur dioxide, oxalic acid, ferrous sulphate, formic acid and ethyl alcohol, also yield the blue vanadyl salts (compare Molybdates, Section **VII, 4**). The reaction takes place slowly in the cold, but more rapidly on warming.

2. **Zinc, Cadmium or Aluminium in Acid Solution.**—These carry the reduction still further. The solutions turn at first blue (vanadyl salt—quadrivalent vanadium), then green (tervalent vanadium) and finally violet (bivalent vanadium).

3. **Ammonium Sulphide Solution.**—The solution is coloured brown, due to the formation of thiovanadates. Upon acidification of the solution, brown vanadium sulphide V_2S_5 is incompletely precipitated, and the filtrate usually has a blue colour. The precipitate is soluble in solutions of alkalis, alkali carbonates and sulphides.

4. **Hydrogen Peroxide.**—A red colouration, due to pervanadic acid HVO_4, is produced when a *few drops* of hydrogen peroxide solution are added to an acid (15–20% sulphuric acid) solution of a vanadate. The colour is not removed by shaking the solution with ether nor is affected by phosphates or fluorides (distinction from titanium).

Recent work supports the view that the red colour is due to the per-salt $(VO_2)_2(SO_4)_3$, which is converted by excess of hydrogen peroxide into the yellow ortho peroxy-vanadic acid $(VO_2)(OH)_3$, hence excess of hydrogen peroxide must be avoided.

$$(VO_2)_2(SO_4)_3 + 6H_2O \underset{H_2SO_4}{\overset{H_2O_2}{\rightleftharpoons}} 2(VO_2)(OH)_3 + 3H_2SO_4.$$

† The spot-test technique is as follows. Mix a drop of 15–20 per cent sulphuric acid and a drop of the test solution either on a spot plate or in a porcelain micro-crucible. After a few minutes add 1 drop of 1 per cent hydrogen peroxide solution and then another drop, if necessary. A red to pink colouration appears.

Sensitivity: 2·5 μg. V. Concentration limit: 1 in 20,000.

Molybdates, chromates, iodides, bromides, ceric salts and also large amounts of coloured metallic salts reduce the sensitivity of the reaction.

5. **Ammonium Chloride.**—The addition of solid ammonium chloride to a solution of an alkali vanadate results in the separation of colourless, crystalline ammonium vanadate NH_4VO_3, sparingly soluble in a concentrated solution of ammonium chloride.

6. **Lead Acetate Solution**: yellow precipitate of lead vanadate, appreciably soluble in nitric acid, and turning white on standing.

7. **Barium Chloride Solution**: yellow precipitate of barium vanadate (distinction from arsenate and phosphate), soluble in dilute hydrochloric acid.

8. **Copper Sulphate Solution**: green precipitate with metavanadates. Pyro-vanadates give a yellow precipitate.

9. **Mercurous Nitrate Solution**: white precipitate of mercurous vanadate from neutral solutions.

10. **Ammonium Hydroxide Solution.**—When this reagent is added to a solution of a salt containing quadrivalent vanadium (*e.g.*, that produced by reduction of a vanadate with hydrogen sulphide), dark grey hypovanadic acid H_2VO_3 is formed; the precipitation is not complete unless excess of ferric chloride be present.

11. **Cupferron Reagent**: deep red precipitate in dilute acid solution.

12. **Tannin Test.**—When a neutral or acetic acid solution of a vanadate is treated with an excess of 10 per cent tannin solution, a deep blue (or blue-black) colouration is obtained. If ammonium acetate is present, a dark blue (or blue-black) precipitate separates. The precipitate or colouration is destroyed by mineral acids.

† *13.* **Ferric Chloride-Dimethylglyoxime Test.**—The reaction:

$$V^{IV} + Fe^{+++} \rightleftharpoons V^{V} + Fe^{++}$$

proceeds from left to right in alkaline solution and in the reverse direction in acid solution. The test for vanadates utilises the deep red colouration with dimethylglyoxime given by ferrous salts (compare Ferrous Iron, Section **III, 19,** reaction *10*) and the fact that vanadates are readily reduced to the quadrivalent state by heating with concentrated hydrochloric acid:

$$V_2O_5 + 10HCl = 2VCl_4 + Cl_2 + 5H_2O.$$

Evaporate 1 drop of the test solution and 2 drops of concentrated hydrochloric acid in a micro-crucible *almost* to dryness. When cold, add a drop of 1 per cent ferric chloride solution, followed by 3 drops of a 1 per cent alcoholic solution of dimethylglyoxime, and render the mixture alkaline with ammonia solution. Dip a strip of quantitative filter paper or of drop-reaction paper into the solution. The precipitated ferric hydroxide remains behind and the red solution of ferrous dimethylglyoxime diffuses up the capillaries of the paper.

Sensitivity: 1 μg. V. Concentration limit: 1 in 50,000.

Dry Test

Borax bead: oxidising flame—colourless (yellow in the presence of much vanadium); reducing flame—green.

Separation.—Vanadates are not precipitated by H_2S in acid solution; reduction to the quadrivalent state occurs. With ammonium sulphide solution, the soluble thio-salt is formed, from which brown V_2S_5 is precipitated by pouring into $6N$ H_2SO_4. The precipitate may be dissolved in concentrated HCl, and tests *4* and *12* applied.

In general, however, the vanadyl salt present in the filtrate from Group II will be largely re-oxidised to vanadate by the nitric acid treatment before the precipitation of Group IIIA. If the solution contains the cations of Group IIIA and certain members of later groups, the vanadates of these metals may be precipitated. However, if no other member of Group IIIA is present, vanadium may be incompletely precipitated as ammonium vanadate. It is therefore recommended where vanadium is suspected (pale-blue solution left after the passage of hydrogen sulphide in Group II) that the Group II filtrate be tested for iron with potassium ferrocyanide solution. If iron is absent, some ferric chloride solution should be added before precipitation of Group IIIA.

See also Table XLV in Section **VII, 17.**

BERYLLIUM (OR GLUCINUM), Be

Beryllium is a divalent metal and closely resembles aluminium in chemical properties; it also exhibits resemblances to the alkaline earth metals. The salts react acid in aqueous solution, and possess a sweet taste (hence the name glucinum formerly given to the element).

VII, 11. REACTIONS OF BERYLLIUM COMPOUNDS

Use a solution of beryllium sulphate, $BeSO_4,4H_2O$.

1. **Ammonium Hydroxide or Ammonium Sulphide Solution**: white precipitate of beryllium hydroxide $Be(OH)_2$, similar in appearance to aluminium hydroxide, insoluble in excess of the reagent, but readily soluble in dilute hydrochloric acid, forming a colourless solution.

2. **Sodium Hydroxide Solution**: white gelatinous precipitate of beryllium hydroxide, readily soluble in excess of the precipitant, forming sodium beryllate $Na_2[BeO_2]$; on boiling the latter solution (best when largely diluted), beryllium hydroxide is reprecipitated (distinction from aluminium). The precipitate is also soluble in 10% sodium bicarbonate solution (distinction from aluminium).

$$Be(OH)_2 + 2NaOH \rightleftharpoons Na_2[BeO_2] + 2H_2O.$$

On the other hand, the precipitate is insoluble in aqueous ethylamine solution whereas aluminium hydroxide dissolves in a moderate excess of the reagent.

3. **Ammonium Carbonate Solution** : white precipitate of beryllium carbonate $BeCO_3$, soluble in excess of the reagent (difference from aluminium). On boiling the solution, the beryllium is precipitated as the white basic carbonate.

4. **Oxalic Acid or Ammonium Oxalate Solution** : no precipitate (difference from thorium and cerium).

5. **Sodium Thiosulphate Solution** : no precipitate (difference from aluminium).

6. **Basic Acetate—Chloroform Test.**—Upon dissolving beryllium hydroxide (reaction *1*) in glacial acetic acid and evaporating to dryness with a little water, basic beryllium acetate $BeO,3Be(C_2H_3O_2)_2$ is produced, which dissolves readily upon extraction with chloroform. This forms the basis of a method for separating beryllium from aluminium, since basic aluminium acetate is insoluble in chloroform. The mixed hydroxides are treated as detailed above.

† *7.* **Quinalizarin Reagent*** : cornflower-blue colouration with faintly alkaline solutions of beryllium salts. The reagent alone gives a characteristic violet colour with dilute alkali; but this is quite distinct from the blue of the beryllium complex : a blank test will render the difference clearly apparent.

Antimony, zinc and aluminium salts do not interfere ; aluminium should, however, be kept in solution by the addition of sufficient sodium hydroxide ; the influence of copper, nickel and cobalt salts can be eliminated by the addition of potassium cyanide solution ; iron salts are " masked " by the addition of a tartrate but if aluminium salts are also present a red colour is produced. Magnesium salts give a similar blue colour, but beryllium can be detected in the presence of this element by utilising the fact that in ammoniacal solution the magnesium colour alone is completely destroyed by bromine water.

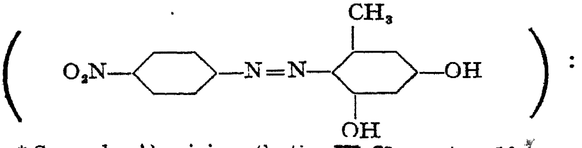
In adjacent depressions of a spot plate place a drop of the test solution and a drop of distilled water, and add a drop of the freshly-prepared quinalizarin reagent to each. A blue colouration, quite distinct from the violet colour of the reagent, is obtained.

Sensitivity : 0·15 μg. Be. Concentration limit : 1 in 350,000.

If **magnesium is present,** treat a drop of the solution on a spot plate with 2 drops of the reagent and 1 c.c. of saturated bromine water. The original deep blue colour becomes paler when the bromine is added, but remains more or less permanently blue.

The **reagent** is prepared by dissolving 0·05 g. of quinalizarin in 100 c.c. of 0·1*N*-sodium hydroxide.

† 8. **para-Nitrobenzene-azo-orcinol Reagent**



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* See under Aluminium, Section **III, 21,** reaction *10.*

orange-red lake with beryllium salts in alkaline solution. Magnesium salts yield a brownish-yellow precipitate; salts and hydroxides of the rare earths, aluminium and alkaline earths are without influence; the interfering effect of silver, copper, cadmium, nickel, cobalt and zinc is eliminated by the addition of potassium cyanide solution.

Place a drop of the reagent on drop-reaction paper and into the middle of the resultant yellow area introduce the tip of a capillary containing the test solution so that the latter runs slowly on to the paper. Treat the stain with a further drop of the reagent. The stain is coloured deep orange-red.

Sensitivity: 0·2 μg. Be. Concentration limit: 1 in 200,000.

The **reagent** consists of a 0·025 per cent solution of *p*-nitrobenzene-azo-orcinol in *N*-sodium hydroxide.

Dry Test

Upon heating beryllium salts with a few drops of cobalt nitrate solution upon charcoal, a grey mass is obtained (difference from aluminium).

Separation.—Beryllium is precipitated in Group IIIA. It is ultimately associated with aluminium in solution as sodium aluminate and sodium beryllate respectively. Upon diluting and boiling, only the $Be(OH)_2$ is precipitated. Alternatively, the quinalizarin test *7* may be applied to the solution or the basic acetate-chloroform test *6* to the mixed hydroxides.

Aluminium and beryllium are most satisfactorily separated by means of 8-hydroxyquinoline ("oxine") reagent; aluminium "oxinate" is precipitated in the presence of an ammonium acetate-acetic acid buffer solution, whereas beryllium "oxinate" is soluble in acetic acid. For this purpose, the alcoholic solution of the reagent (compare Magnesium, Sect. **III, 33**, reaction 7) should not be employed as the aluminium complex is slightly soluble in alcohol. The solution of sodium aluminate and beryllate is just acidified with dilute hydrochloric acid, a slight excess of the "oxine" solution added, followed by 5 c.c. of saturated ammonium acetate solution. The precipitate of the aluminium complex $Al(C_9H_6ON)_3$ is filtered off. The filtrate is heated nearly to boiling and a slight excess of ammonia solution added. The production of a precipitate (beryllia), usually coloured brown or yellow by adsorbed "oxine," indicates the presence of beryllium.

The *precipitating reagent* consists of a 2% solution of "oxine" in 2*N*-acetic acid to which ammonia solution is added until a permanent precipitate is produced, and the latter is re-dissolved by warming.

Another method for separating beryllium and aluminium consists in adding excess of a solution of sodium fluoride to the solution. The complex sodium alumino-fluoride $Na_3[AlF_6]$ is formed in which the aluminium is present as a complex ion and from which the metal is not precipitated as hydroxide by ammonia solution. Beryllium is, however, readily precipitated as the hydroxide under these conditions.

See also *Note 6* to Table XLV in Section **VII, 17.**

TITANIUM, Ti

The most important compounds of titanium are those corresponding to the two oxides TiO_2 and Ti_2O_3. The latter, containing trivalent titanium (titanous compounds), usually yield violet aqueous solutions, and are powerful reducing agents: they behave like iron and aluminium towards the common reagents. The salts of quadrivalent titanium (titanic compounds) are usually colourless, and are more frequently encountered in analytical work.

VII, 12. REACTIONS OF TITANIC COMPOUNDS

Use a solution of titanic sulphate, $Ti(SO_4)_2$*.

1. **Solutions of Sodium Hydroxide, Ammonium Hydroxide or Ammonium Sulphide.**—All these reagents give a white gelatinous precipitate of ortho-titanic acid H_4TiO_4 or $Ti(OH)_4$ in the cold, almost insoluble in excess of the reagent, but soluble in mineral acids. If precipitation takes place from hot solution, meta-titanic acid H_2TiO_3 or $TiO.(OH)_2$ is formed, which is difficultly soluble in dilute acids.

2. **Water.**—A white precipitate of meta-titanic acid is obtained on boiling a solution of a titanic salt with excess of water.

3. **Sodium Phosphate Solution**: white precipitate of titanium phosphate $Ti(HPO_4)_2$ in dilute sulphuric acid solution.

4. **Zinc or Tin.**—When either of these metals is added to an acid (preferably hydrochloric acid) solution of a titanic salt, a violet colouration is produced, due to reduction to the titanous state. No reduction occurs with sulphur dioxide or with hydrogen sulphide.

5. **Cupferron Reagent****: flocculent yellow precipitate of the titanium salt, $Ti(C_6H_5O_2N_2)_4$, in acid solution (distinction from aluminium and beryllium). If *iron is present*, it can be removed by precipitation with ammonia and ammonium sulphide solutions in the presence of a tartrate; the titanium may then be precipitated from the acidified solution by cupferron.

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* This may be prepared by fusing the dioxide TiO_2 with a large excess of potassium pyrosulphate $K_2S_2O_7$. The melt, after powdering, is extracted with *cold* water or with cold dilute H_2SO_4 and filtered, if necessary.

$$TiO_2 + 2K_2S_2O_7 = Ti(SO_4)_2 + 2K_2SO_4.$$

** For the preparation of the reagent, see under Iron, Section **III, 20,** reaction *9*.

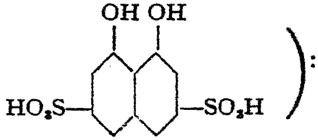
6. **Hydrogen Peroxide.**—An orange-red colouration is produced in slightly acid solution. The colour is yellow with very dilute solutions. The colouration was formerly attributed to TiO_3, but recent work has shown that it is more probably due to peroxo-disulphato-titanic acid $H_2[TiO_2(SO_4)_2]$.

Chromates, vanadates, molybdates and cerium salts give colour reactions with the reagent and should therefore be absent. Iron salts give a violet colour with hydrogen peroxide, but this is destroyed by the addition of syrupy phosphoric acid. Fluorides bleach the colour (stable $[TiF_6]^{--}$ ions formed), and large amounts of nitrates, chlorides, bromides and acetates as well as coloured ions reduce the sensitivity of the test.

† The spot-test technique is as follows. Place a drop of the sulphuric acid test solution on a spot plate and add a drop of " 10-volume " hydrogen peroxide. A yellow colouration results.

Sensitivity : 2μg. Ti. Concentration limit : 1 in 25,000.

† *7*. **Chromotropic Acid** Reagent**



reddish-brown colouration with titanium salts in the presence of hydrochloric or sulphuric acid. Appreciable concentrations of nitric acid inhibit the reaction.

Mix a drop of the test solution and a drop of the reagent on drop-reaction paper or upon a spot plate. A reddish-brown spot or colouration results.

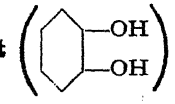
Sensitivity : 5 μg. TiO_2. Concentration limit : 1 in 10,000.

Uranyl and ferric salts interfere and yield brown and deep green colourations respectively ; these colours are destroyed by the addition of stannous chloride for uranous and ferrous salts do not react with chromotropic acid. Mercury salts give a yellow and silver salts a black stain on drop-reaction paper ; the colour due to titanium is, however, still perceptible.

In the **presence of uranyl salts and/or ferric salts,** proceed as follows. Mix a large drop of the test solution on a watch glass with a small quantity of a solution of stannous chloride in hydrochloric acid (a large excess is to be avoided) and warm gently (hot plate). Place a drop of the reagent on some drop-reaction paper and then a drop of the clear solution from the watch glass. A reddish-brown spot appears.

The **reagent** consists of a 5 per cent aqueous solution of chromotropic acid.

† *8*. **Pyrocatechol Reagent**



: yellow colouration with

** Or 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid.

neutral or weakly acid (sulphuric acid) solutions of titanium salts. Ferric, chromium, cobalt and nickel salts interfere as do also large amounts of free mineral acids : alkali hydroxides and carbonates reduce the sensitivity of the test.

Place a drop of the sulphuric acid test solution on drop-reaction paper impregnated with the reagent. A yellow or yellowish-red spot is obtained.

Sensitivity : 3 μg. Ti. Concentration limit : 1 in 20,000.

The **reagent** consists of a freshly-prepared 10 per cent aqueous solution of pyrocatechol.

Dry Test

Microcosmic salt bead : oxidising flame—colourless ; reducing flame—yellow whilst hot and violet when cold (this result is obtained more rapidly if a little stannous chloride is added).

Separation.—If sufficient acid is present in the earlier groups to prevent its separation by hydrolysis, titanium is found in Group IIIA. It can be readily detected in the precipitate obtained after treatment with Na_2O_2 by means of the hydrogen peroxide test *4* ; NaF solution will discharge the colour. It is usually best to fuse the precipitate with 10 times its weight of powdered $K_2S_2O_7$ or $KHSO_4$; the melt, containing the metals as sulphates, is extracted with cold water, and the extract boiled for about 30 minutes. Meta-titanic acid separates out. This is filtered off, dissolved in concentrated HCl, and the H_2O_2 test applied.

See also Table XLV in Section **VII, 17.**

VII, 18. REACTIONS OF ZIRCONIUM COMPOUNDS

Zirconium* forms only one important oxide, zirconia ZrO_2, which is amphoteric in character. The normal zirconium salts, like $ZrCl_4$, are readily hydrolysed in solution giving rise chiefly to zirconyl salts, containing the bivalent radical ZrO^{II}. The zirconates, *e.g.*, Na_2ZrO_3, are best produced from ZrO_2 by fusion methods. Zirconium also readily forms complex salts, *e.g.*, potassium fluozirconate $K_2[ZrF_6]$, produced by fusing zirconia with potassium hydrogen fluoride.

Ignited zirconium dioxide, or the mineral, is insoluble in all acids except hydrofluoric acid. It is soluble in fused caustic alkalis and in sodium carbonate ; the resultant alkali zirconate is practically insoluble in water, being converted into zirconium hydroxide by this solvent. It is therefore best dissolved in hydrochloric acid, and the zirconium precipitated by ammonia solution, etc.

Use a solution of zirconium nitrate $Zr(NO_3)_4$ (or $ZrO(NO_3)_2$) or of zirconyl chloride $ZrOCl_2,8H_2O$.

1. **Sodium Hydroxide Solution** : white gelatinous precipitate of the hydroxide $Zr(OH)_4$ (or ZrO_2,xH_2O) in the cold, practically insoluble in excess of the reagent (difference from aluminium and beryllium), but soluble in dilute mineral acids (avoid sulphuric acid). With a hot solution of a zirconium salt, a white precipitate of $ZrO(OH)_2$ is obtained ; it is sparingly soluble in dilute but soluble in concentrated mineral acids.

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* Small quantities of hafnium are always present ; the two elements cannot, at present, be differentiated by qualitative analysis.

2. **Ammonium Hydroxide or Ammonium Sulphide Solution** : white gelatinous precipitate of the hydroxide $Zr(OH)_4$ (or ZrO_2,xH_2O), insoluble in excess of the reagent.

3. **Sodium Phosphate Solution** : white precipitate of zirconium phosphate, $Zr(HPO_4)_2$ or $ZrO(H_2PO_4)_2$, even in solutions containing 10 per cent of sulphuric acid by weight. No other element forms an insoluble phosphate under these conditions except titanium. The latter element can be kept in solution as the so-called " per-titanic acid " by the addition of sufficient hydrogen peroxide solution, preferably of " 100-volume " strength, before the sodium phosphate is introduced.

4. **Hydrogen Peroxide** : white precipitate of zirconium " peroxide " from slightly acid solutions ; this liberates chlorine when warmed with concentrated hydrochloric acid. When both hydrogen peroxide and sodium phosphate are added to a solution containing zirconium, the precipitate is zirconium phosphate (see reaction *3*).

5. **Ammonium Carbonate Solution** : white precipitate of basic zirconium carbonate, readily soluble in excess of the reagent, but reprecipitated on boiling.

6. **Oxalic Acid Solution** : white precipitate of zirconium oxalate, readily soluble in excess of the reagent and also in ammonium oxalate solution (difference from thorium).

7. **Ammonium Oxalate Solution** : white precipitate of zirconium oxalate, soluble in excess of the reagent (distinction from aluminium and beryllium) ; the solution gives no precipitate with hydrochloric acid (difference from thorium).

Note. A solution of zirconium sulphate or a zirconium salt solution containing excess of sulphate ions does not give a precipitate with either ammonium oxalate or oxalic acid. This is due to the fact that the zirconium is present as the anion $[ZrO(SO_4)_2]^{--}$, hence sulphuric acid should be avoided in preparing solutions of zirconium salts.

8. **Saturated Potassium Sulphate Solution** : white precipitate of $K_2[ZrO(SO_4)_2]$, insoluble in excess. When precipitation takes place in boiling solution, the resultant basic zirconium sulphate is insoluble in dilute hydrochloric acid (difference from thorium and cerium). No precipitate is obtained with sodium sulphate solution.

9. **Phenylarsonic Acid Reagent** { $C_6H_5.AsO(OH)_2$ } : white precipitate of zirconium phenylarsonate in the presence of 0·5-1*N*-hydrochloric acid ; it is best to boil the solution. Tin and thorium salts must be absent.

The *reagent* consists of a 10 per cent aqueous solution of phenylarsonic acid.

10. **normal-Propylarsonic Acid Reagent** $\{CH_3.CH_2.CH_2.AsO(OH)_2\}$: white precipitate of zirconium *n*-propylarsonate in dilute sulphuric acid solution (separation from most other metals including titanium but not tin).

The *reagent* consists of a 5 per cent aqueous solution of *n*-propylarsonic acid.

11. **Alizarin-S* Reagent**: violet-red colouration on gentle warming, best in *N*-hydrochloric acid solution, due to the formation of a zirconium-alizarin mordant dye. Fluorides discharge the colour because of the formation of the stable zirconi-fluoride anion $[ZrF_6]^{--}$. Phosphates, oxalates and sulphates interfere.

The *reagent* consists of a 0·1 per cent aqueous solution of alizarin-S (sodium alizarin sulphonate).

† *12.* **Alizarin* Reagent**: red-brown to dark violet precipitate in acid solution, particularly on warming. Fluorides, phosphates, sulphates, molybdates, tungstates, and organic hydroxy-acids interfere because of either precipitation or complex-ion formation.

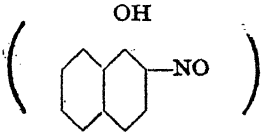
Mix a drop of the nearly neutral test solution with a drop of the reagent in a micro-crucible and heat just to boiling. A red to violet colouration is produced. Add a drop of *N*-hydrochloric acid; only the zirconium compound remains unaffected and a red-violet colour and precipitate (or, for small quantities of zirconium, reddish-brown flecks) are obtained.

Sensitivity: 0·5 μg. Zr. Concentration limit: 1 in 100,000.

This procedure is applicable in the presence of beryllium, aluminium, titanium and thorium salts; the sensitivity is 1·5 μg. Zr in the presence of 500 times the amount of Al, and 1·0 μg. Zr in the presence of 500 times the amount of Th.

The **alizarin reagent** is prepared by treating an alcoholic solution of commercial alizarin dropwise with dilute hydrochloric acid until a pure yellow colour develops, then adding an equal volume of alcohol and filtering.

† *13.* **β-Nitroso-α-naphthol Reagent**



Hydrochloric acid solutions of zirconium salts give a deep red colour with the reagent; precipitation occurs if sodium acetate is added. Large amounts of fluorides and sulphates hinder the reaction; the interference of sulphates is prevented by the addition of barium chloride solution.

Impregnate a piece of drop-reaction paper with the reagent, and dry the paper. Add a drop of the hydrochloric acid test solution. A deep red spot is formed on the yellowish-brown paper.

Sensitivity: 0·2 μg. Zr. Concentration limit: 1 in 250,000.

The **reagent** consists of a 2 per cent solution of β-nitroso-α-naphthol in alcohol.

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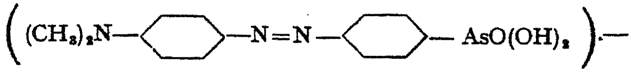
* For formula, etc., see under Aluminium, Section **III, 21.**

†*14*. para-Dimethylaminobenzene-azo-phenylarsonic Acid Reagent



Acid solutions of zirconium salts give a brown precipitate with the reagent. If the test be conducted on filter paper, the brown precipitate remains in the pores of the paper and the excess of the coloured reagent may be washed out with dilute acid.

Impregnate some drop-reaction paper with the reagent and dry the paper. Place a drop of the acid test solution on the paper. Dip the paper into 2*N*-hydrochloric acid at 50°–60°C. A brown spot or ring remains.

Sensitivity : 0·1 μg. Zr (in *N*-HCl). Concentration limit : 1 in 500,000.

Free sulphuric acid exceeding *N* in concentration reduces the sensitivity of the test ; phosphates, fluorides and organic acids, which form precipitates or stable complex compounds, either inhibit or retard the reaction ; molybdates, tungstates and salts of titanium or cerium give precipitates, but their interference can be eliminated by mixing the test solution with about an equal volume of concentrated hydrochloric acid, adding some " 100-volume " hydrogen peroxide, spotting the mixture on to impregnated drop-reaction paper and finally washing the latter with warm 2*N*-hydrochloric acid. Tin also gives a coloured precipitate, but this may be prevented by the above treatment and omitting the hydrogen peroxide ; a brown ring, surrounding a central zone, is obtained.

The **reagent** is prepared by dissolving 0·1 g. of *p*-dimethylaminobenzene-azo-phenylarsonic acid in 5 c.c. of concentrated hydrochloric acid and 100 c.c. of alcohol.

Dry Tests

No characteristic results are obtained with the borax or microcosmic beads nor does zirconium yield a distinguishing flame test.

Separation.—Zirconium is precipitated in Group IIIA as ZrO_2, xH_2O, if phosphates are absent. It can be readily detected in the residue obtained after treating the Group IIIA precipitate with 10 per cent sodium hydroxide solution and " 20 or 40-volume " hydrogen peroxide. The residue is dissolved in hydrochloric acid and boiled to expel chlorine. The resultant solution is treated with sodium phosphate solution and hydrogen peroxide, when a white precipitate indicates the presence of *zirconium* and an orange-yellow colouration the presence of *titanium* (see reaction *3* above). Alternatively, the alizarin-S test (reaction *11*) may be applied to the solution in hydrochloric acid.

See also Table XLV in Section **VII, 17.**

Uranium, U

The most important uranium compounds are the uranyl salts, which contain the bivalent radical uranyl $UO_2<$, and the uranates $M_2U_2O_7$, analogous to the pyrosulphates $M_2S_2O_7$ and the dichromates $M_2Cr_2O_7$. Only the reactions of the former will be described.

VII, 14. REACTIONS OF URANYL COMPOUNDS

Use a solution of uranyl nitrate, $UO_2(NO_3)_2,6H_2O$, or of uranyl acetate, $UO_2(C_2H_3O_2)_2,2H_2O$.

1. **Ammonium Hydroxide Solution**: yellow precipitate of ammonium uranate $(NH_4)_2U_2O_7$, insoluble in excess of the reagent, but readily soluble in ammonium carbonate solution.

$$2UO_2(NO_3)_2 + 6NH_4OH = (NH_4)_2U_2O_7 + 4NH_4NO_3 + 3H_2O.$$

$$(NH_4)_2U_2O_7 + 6(NH_4)_2CO_3 + 3H_2O = 2(NH_4)_4[UO_2(CO_3)_3] + 6NH_4OH.$$

No precipitation occurs in the presence of certain organic acids, such as tartaric and citric acids.

2. **Sodium Hydroxide Solution**: yellow amorphous precipitate of sodium uranate $Na_2U_2O_7$, soluble in ammonium carbonate solution.

3. **Ammonium Sulphide Solution**: brown precipitate of uranyl sulphide UO_2S, soluble in dilute acids and in ammonium carbonate solution.

4. **Hydrogen Peroxide**: pale-yellow precipitate of UO_4,xH_2O, soluble in ammonium carbonate solution with the formation of a deep yellow solution. Chromium, titanium and vanadium interfere with this otherwise sensitive test.

5. **Cupferron Reagent**: no precipitate (distinction from titanium).

6. **Sodium Phosphate Solution**: white precipitate of uranyl ammonium phosphate $UO_2(NH_4)PO_4$ in the presence of ammonium sulphate or acetate, insoluble in acetic acid but soluble in mineral acids.

7. **Ammonium Carbonate Solution**: white precipitate of uranyl carbonate UO_2CO_3, soluble in excess of the reagent forming a clear yellow solution containing ammonium uranyl carbonate $(NH_4)_4[UO_2(CO_3)_3]$.

8. **Potassium Ferrocyanide Solution**: brown precipitate of uranyl ferrocyanide $(UO_2)_2[Fe(CN)_6]$ in neutral or acetic acid solutions, soluble in dilute hydrochloric acid (difference from copper). The precipitate becomes yellow upon the addition of sodium hydroxide solution, due to its conversion into sodium uranate (distinction from copper and from molybdenum ferrocyanide).

$$(UO_2)_2[Fe(CN)_6] + 6NaOH = Na_2U_2O_7 + Na_4Fe(CN)_6 + 3H_2O.$$

† The spot-test technique is as follows. Place a drop of the test solution on drop-reaction paper and add a drop of potassium ferrocyanide solution. A brown spot is obtained.

Sensitivity: 0·9 μg. U. Concentration limit: 1 in 50,000.

Both iron and copper interfere. If, however, potassium iodide solution is added, they are reduced to the non-reactive ferrous and cuprous states; the liberated iodine may be decolourised with sodium thiosulphate solution. Alternatively, the reduction may be carried out with sodium thiosulphate solution alone on a spot plate, the copper acting as a catalyst for the reduction of the iron:

$$2Fe^{+++} + 2S_2O_3^{--} = 2Fe^{++} + S_4O_6^{--};$$
$$2Cu^{++} + 2S_2O_3^{--} = Cu_2^{++} + S_4O_6^{--}.$$

Place a drop of concentrated potassium iodide solution on a piece of drop-reaction paper and, after the iodide solution has soaked into the paper, add a drop of the acidified test solution. Add a further drop of the potassium iodide solution to complete the reduction, followed by a drop of sodium thiosulphate solution. Then add a drop of potassium ferrocyanide solution to the decolourised spot, whereupon a brown ring is obtained.

Dry Test

Borax or microcosmic salt bead: oxidising flame—yellow; reducing flame—green.

Separation.—Uranium is precipitated in Group IIIA as $(NH_4)_2U_2O_7$. It is most simply separated from $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$ by digestion in the cold with a large excess of ammonium carbonate solution. The ammonium uranate dissolves (see reaction *1* above); upon acidification with HCl and addition of $K_4[Fe(CN)_6]$ solution, a brown precipitate is formed.

See also Table XLV in Section **VII, 17.**

THORIUM, Th

The analytically important compounds of thorium are derived from the dioxide ThO_2, *i.e.*, contain quadrivalent thorium.

VII, 15. REACTIONS OF THORIUM COMPOUNDS

Use a solution of thorium nitrate, $Th(NO_3)_4,xH_2O$.

1. **Ammonium Hydroxide, Ammonium Sulphide or Sodium Hydroxide Solution**: white precipitate of thorium hydroxide $Th(OH)_4$, insoluble in excess of the reagent, but readily soluble in dilute acids when freshly precipitated.

2. **Ammonium Carbonate Solution**: white precipitate of basic carbonate, readily soluble in excess of the concentrated reagent.

3. **Oxalic Acid Solution**: white, crystalline precipitate of thorium oxalate $Th(C_2O_4)_2,6H_2O$ (distinction from aluminium and beryllium), insoluble in excess.

4. **Ammonium Oxalate Solution**: white precipitate of thorium oxalate, which dissolves on boiling with a large excess of the reagent, but is reprecipitated upon the addition of hydrochloric acid (difference from zirconium).

5. **Saturated Potassium Sulphate Solution**: white precipitate of double salt, $2K_2SO_4,Th(SO_4)_2,2H_2O$.

6. **Hydrogen Peroxide**: white precipitate of hydrated thorium peroxide in neutral or faintly acid solution.

7. **Sodium Thiosulphate Solution**: precipitate of thorium hydroxide and sulphur on boiling (distinction from cerium).

8. **Potassium Iodate Solution**: white, bulky precipitate of thorium iodate $Th(IO_3)_4$. Precipitation occurs in the presence of 50% by volume of concentrated nitric acid.

9. **Potassium Ferrocyanide Solution**: white precipitate of thorium ferrocyanide $Th[Fe(CN)_6]$ in neutral or slightly acid solution.

10. **Potassium Fluoride Solution**: white, bulky precipitate of thorium fluoride ThF_4, insoluble in excess of the reagent (distinction and method of separation from aluminium, beryllium, zirconium and titanium).

11. **Saturated Sebacic Acid Solution** ($CO_2H.(CH_2)_8.CO_2H$): white voluminous precipitate of thorium sebacate $Th(C_{10}H_{16}O_4)_2$ (difference from cerium).

12. **meta-Nitrobenzoic Acid Reagent** ($NO_2.C_6H_4.CO_2H$).—Upon addition of excess of the reagent to a neutral solution of a thorium salt at about 80°, a white precipitate of the salt $Th(NO_2.C_6H_4.CO_2)_4$ is obtained (distinction from cerium).

The *reagent* is prepared by dissolving 1 gram of the acid in 250 c.c. of water at 80°, allowing to cool overnight and filtering.

There are no characteristic dry tests for thorium.

Separation.—See under Cerium (Section **VII, 16**).

CERIUM, Ce

Cerium forms two well-defined series of salts, cerous and ceric, in which the element is tervalent and quadrivalent respectively. The cerium is more basic in the former than in the latter state, hence the cerous salts are the more stable.

VII, 16A. REACTIONS OF CEROUS COMPOUNDS

Use a solution of cerous nitrate, $Ce(NO_3)_3,xH_2O$.

1. **Ammonium Hydroxide or Ammonium Sulphide Solution**: *white* precipitate of cerous hydroxide $Ce(OH)_3$, insoluble in excess of the precipitant, but readily soluble in acids. The precipitate slowly oxidises in the air, finally becoming converted into yellow ceric hydroxide $Ce(OH)_4$. Sodium hydroxide solution gives a similar result.

2. **Oxalic Acid or Ammonium Oxalate Solution**: white precipitate of cerous oxalate $Ce_2(C_2O_4)_3$, insoluble in excess of the reagent (compare thorium and zirconium), and in dilute mineral acids.

3. **Sodium thiosulphate Solution**: no precipitate (distinction from thorium).

4. **Saturated Potassium Sulphate Solution**: white, crystalline precipitate, having the composition $Ce_2(SO_4)_3,3K_2SO_4$ in neutral solution and $Ce_2(SO_4)_3,2K_2SO_4,2H_2O$ from slightly acid solution (difference from aluminium and beryllium).

5. **Sodium Bismuthate.**—This reagent converts cerous into ceric salts in the cold. A similar result is obtained by heating with ammonium persulphate or with lead dioxide and dilute nitric acid (1:2). In all cases, the solutions become yellow or orange in colour.

6. **Ammonium Carbonate Solution**: white precipitate of cerous carbonate $Ce_2(CO_3)_3$, nearly insoluble in excess of the precipitant (difference from beryllium, thorium and zirconium) and insoluble in sodium carbonate solution.

7. **Hydrogen Peroxide.**—When a cerous salt is treated with ammonium hydroxide solution and excess of hydrogen peroxide is added a yellowish-brown or reddish-brown precipitate or colouration, due to cerium per-hydroxide $Ce(OH)_3(OOH)$, is formed. This is not very stable. Upon boiling the mixture, yellow ceric hydroxide $Ce(OH)_4$ is obtained. The test cannot be applied directly in the presence of iron since the colour of ferric hydroxide is similar to that of ceric per-hydroxide. The precipitation of ferric hydroxide may be prevented by the addition of an alkali tartrate in consequence of the formation of complex ferri-tartrate ions; this, however, reduces the sensitivity of the test for cerium.

† The spot-test technique is as follows. Mix a drop of the hot test solution, of "10-volume" hydrogen peroxide and of dilute ammonia solution in a porcelain micro-crucible and warm gently. A yellow or yellowish-brown precipitate or colouration appears.

Sensitivity: 0·35 μg. Ce. Concentration limit: 1 in 140,000.

† *8.* **Ammoniacal Silver Nitrate Reagent.**—This reagent reacts with neutral solutions of cerous salts to form ceric hydroxide and metallic silver; the former is coloured black by the finely-divided silver:

$$Ce(OH)_3 + [Ag(NH_3)_2]^+ + OH^- = Ce(OH)_4 + Ag + 2NH_3.$$

Ferric, manganous and cobaltous salts also give the higher metallic hydroxides and silver, and must therefore be absent.

Mix a drop of the neutral test solution and a drop of the reagent on a watch glass or in a porcelain micro-crucible, and warm gently. A black precipitate or brown colouration appears.

Sensitivity: 1 μg. Ce. Concentration limit: 1 in 50,000.

The **ammoniacal silver nitrate reagent** is prepared by treating *ca.* 0·4*N*-silver nitrate with dilute ammonia solution until the precipitate first formed is just redissolved.

VII, 16B. REACTIONS OF CERIC COMPOUNDS

Use a solution of ceric ammonium sulphate $Ce(SO_4)_2,2(NH_4)_2SO_4,2H_2O$ or of ceric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]H_2O$ (or $Ce(NO_3)_4,2NH_4NO_3,H_2O$).

1. **Ammonium or Sodium Hydroxide Solution** : *yellow* precipitate of ceric hydroxide $Ce(OH)_4$. If the precipitate is warmed with hydrochloric acid, chlorine is evolved and cerous chloride is formed.

2. **Oxalic Acid or Ammonium Oxalate Solution** : reduction occurs, more rapidly on warming, to the cerous condition, and ultimately white cerous oxalate is precipitated.

3. **Saturated Potassium Sulphate Solution** : no precipitate (distinction from cerous salts).

4. **Reducing Agents** (*e.g.*, Hydrogen Sulphide, Sulphur Dioxide, Hydrogen Peroxide and Hydriodic Acid).—These convert ceric salts into cerous salts.

Dry Test

Borax Bead : oxidising flame—dark brown whilst hot and light yellow to colourless when cold ; reducing flame—colourless.

Separation.—Cerium and thorium salts are precipitated in Group IIIA. They may be separated from the other metals of the group by dissolving the precipitate in dilute HCl and adding oxalic acid solution, when the oxalates of both metals are precipitated. The thorium and cerium may be separated : (*a*) by dissolving the thorium oxalate in a mixture of ammonium acetate solution and acetic acid, cerium oxalate being insoluble under these conditions ; (*b*) by treatment with a large excess of hot concentrated ammonium oxalate solution ; only the thorium oxalate dissolves (a complex ion being formed), and may be reprecipitated from the resultant solution as oxalate by the addition of hydrochloric acid.

In routine qualitative analysis, it is probably best to boil the mixed oxalates with 5–10% potassium hydroxide solution, thereby converting them into the hydroxides. The precipitate is separated by filtration, dissolved in dilute hydrochloric acid, and the solution divided into two parts :—

(i) **Th.**—Neutralise with ammonia solution, and add the meta-nitro-benzoic acid reagent (reaction *12*) or a warm saturated solution of sebacic acid (reaction *11*). Alternatively, hydrochloric acid is added to the neutral solution until the concentration is about $0{\cdot}3N$, and then sodium pyrophosphate solution. A white precipitate, ThP_2O_7, indicates Th.

(ii) **Ce.**—Identify by the addition of hydrogen peroxide, followed by ammonia solution until the liquid is alkaline. A reddish-brown precipitate indicates Ce (see Section **VII, 16A**, reaction *8*).

The following Table contains a scheme for the identification of the more common " rarer " elements (Ti, Zr, Ce, Th, V and U) in the presence of Fe, Al and Cr. If phosphate is present, it should be removed by the metallic tin or the stannic chloride method (Section **VI, 2**).

VII, 17. Table XLV.—Analysis of Group IIIA in the presence of Ti, Zr, Ce, Th, U and V.

Dissolve the ppt. in the minimum quantity of conc. HCl, and pour the solution into an equal volume of " 20-volume " H_2O_2 rendered strongly alkaline with 10 per cent NaOH solution. Boil for 5 minutes. Filter.

Residue. May contain $Fe(OH)_3$; TiO_2,xH_2O; ZrO_2,xH_2O; ThO_2,xH_2O; CeO_2,xH_2O (and MnO_2,xH_2O).

Dissolve in dilute HCl, boil to expel Cl_2, and divide the solution into several parts.

(i) Add KCNS solution (1). Red colouration.

Fe present.

(ii) If Fe present add sufficient H_3PO_4(2) to decolourise the ferric salt, and then add H_2O_2.

Orange-red colouration, discharged by NaF solution.

Ti present (see Section **VII, 12**).

White ppt.

Zr present (3; see also Section **VII, 13**).

(iii) Add excess of saturated oxalic acid solution.

White ppt.

Th and/or Ce present.

For separation, see Section **VII, 16B.**

(iv) Evaporate to fuming with H_2SO_4 to expel HCl. Cool, dilute and add HNO_3 and a little $NaBiO_3$. Purple colouration.

Mn present.

Filtrate. May contain Na_2CrO_4, $NaAlO_2$, Na_3VO_4 and sodium peruranate (probably Na_2UO_5). Acidify with dilute HNO_3, add excess of $Pb(NO_3)_2$ or $Pb(C_2H_3O_2)_2$ solution, followed by 5 c.c. of saturated $NH_4.C_2H_3O_2$ solution. Filter.

Residue. May contain $PbCrO_4$ and $Pb_3(VO_4)_2$. Dissolve in the minimum volume of 3*N* HNO_3, thoroughly cool the resultant solution and transfer to a small separating funnel. Add an equal volume of amyl alcohol, and a little H_2O_2. Shake well and allow two layers to separate

A blue colouration in the upper layer indicates **Cr present,** and a red to reddish-brown colouration (4) in the lower layer indicates **V present.**

Confirm the presence of V thus. Separate the lower layer, and boil (to destroy the pervanadic acid). Acidify with acetic acid, add ammonium acetate and excess of 10 per cent tannin solution.

Blue-black ppt. or colouration.

Filtrate. May contain $NaAlO_2$ and sodium uranate or peruranate. Pass H_2S to remove all the Pb as PbS. Filter. Boil to expel H_2S, almost neutralise with NH_4OH solution, cool, pour into an excess of conc. $(NH_4)CO_3$ solution, allow to stand and filter.

Residue. $Al(OH)_3$. **Al present.** Confirm by Thenard's blue test (5).

Filtrate. May contain U, probably as $(NH_4)_4[UO_2(CO_3)_3]$ Evaporate to a small bulk (6), acidify with HCl, and add $K_4[Fe(CN)_6]$ solution. Brown ppt. of $UO_2[Fe(CN)_6]$, becoming yellow upon addition of NaOH solution.

U present.

Notes.—(1). The potassium ferrocyanide test is not recommended here when U is present. The NaOH-H_2O_2 separation is not quite quantitative and sufficient U may be present in the precipitate to introduce complications.

(2) The addition of phosphoric acid or of sodium phosphate is essential if Zr is to be tested for, even if Fe is absent (compare Section **VII, 13**, reaction *3*).

(3) If both Ti and Zr are present, the ppt. of zirconium phosphate may be filtered off (best in the presence of a little macerated filter paper—see Section **I, 43**) and the filtrate treated with Na_2SO_3 or with $Na_2S_2O_3$ solution and warmed. The so-called " titanium peroxide " is reduced and titanium phosphate precipitates. It may be necessary to reduce the acidity of the solution somewhat to completely precipitate the titanium.

(4) If much Cr and a little V is present, a second extraction with amyl alcohol may be necessary in order to ensure the complete removal of the Cr, and to render the colouration due to V completely visible.

(5) The dry test is preferable to the " aluminon " reaction, for the latter is not applicable in the presence of Be.

(6) A precipitate that separates here may be (basic) beryllium carbonate. It should be filtered off and tested for Be by the basic acetate-chloroform test (see Section **VII, 11**, reaction *6*).

VII, 18. Notes on the Precipitation and Separation of Group IIIB in the presence of " Rarer " Elements

If **thallium** has been found in Group I, some of it may pass into Group IIIB because of the solubility of thallous chloride in water and be precipitated as Tl_2S. It may be readily detected by the green flame colouration. Thallium is best separated from the other elements of Group IIIB by dissolving the precipitate in dilute nitric acid, boiling to expel hydrogen sulphide, adding a little sulphurous acid solution, and boiling again to remove excess of sulphur dioxide. Upon pouring the solution into excess of aqueous sodium carbonate, the carbonates of cobalt, nickel, manganese and zinc are precipitated and the thallium remains in solution as the soluble thallous carbonate. The precipitated carbonates may be dissolved in dilute hydrochloric acid and the usual precipitation carried out. The thallium in the filtrate can be precipitated by the addition of freshly-prepared colourless ammonium sulphide solution.

If **vanadium and/or molybdenum** have been detected in the earlier groups (as indicated by the production of a blue colouration with hydrogen sulphide in acid solution), these elements may also be found in the filtrate from Group IIIB : a violet-red colour points to vanadium and a reddish-brown colouration to molybdenum. As a general rule, vanadium is generally removed in Group IIIA as iron vanadate and its presence in the Group IIIB filtrate is therefore unlikely. However, when the filtrate from Group IIIB is acidified with acetic acid and boiled, the production of a brown precipitate will indicate the removal of any residual molybdenum, vanadium or nickel in the form of sulphides. If desired, the precipitate may be dissolved in concentrated nitric acid, evaporated to dryness and the residue dissolved in hydrochloric acid. Molybdenum is detected by the ammonium thiocyanate or the potassium xanthate test, and vanadium by the tannin or hydrogen peroxide reactions.

VII, 19. Note on the Detection of Lithium in Group V

This element is readily detected in the residue of Group V by means of the spectroscope (see Section **II, 1,** *4*). Further details of the separation of lithium will be found in Section **III, 37.**

In Table XLVI are collected the colourations produced with the borax bead for different elements and will be useful for reference purposes (compare Section **V, 2,** test (iv)).

Table XLVI.—Borax Bead Tests

Oxidising Flame		*Reducing Flame*		*Metal*
Hot	*Cold*	*Hot*	*Cold*	
1. Green	Blue	Colourless	Opaque red or brown	Copper
2. Yellowish-brown	Yellow	Green	Green	Iron
3. Yellow	Green	Green	Green	Chromium
4. Violet (amethyst)	Amethyst	Colourless	Colourless	Manganese
5. Blue	Blue	Blue	Blue	Cobalt
6. Violet	Reddish-brown	Grey	Grey	Nickel
7. Yellow	Colourless	Brown	Brown	Molybdenum
8. Rose-violet	Rose-violet	Red	Violet	Gold
9. Yellow	Colourless	Yellow	Yellow-brown	Tungsten
10. Yellow	Pale yellow	Green	Bottle-green	Uranium
11. Yellow	Greenish-yellow	Brownish	Emerald-green	Vanadium
12. Yellow	Colourless	Grey	Violet	Titanium
13. Orange-red	Colourless	Colourless	Colourless	Cerium

CHAPTER VIII

SYSTEMATIC QUALITATIVE ANALYSIS OF INORGANIC SUBSTANCES FOR ELEMENTARY STUDENTS *

It is assumed that the student is already familiar with the tests and operations described in Chapters II (Sections **II, 1** and **II, 2**), III and IV as outlined in the course of instruction (Section **A, 4**). If the time available for qualitative analysis is extremely limited, the number of reactions studied may be reduced to those having an *immediate* bearing on the subsequent analysis and are given at the end of this chapter.

The student must realise that the object of qualitative analysis is not simply to detect the constituents of a given mixture ; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose about one gram of material is usually employed for the analysis : the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

Every analysis is divided into three parts :

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions). A special preliminary test for nitrate and/or nitrite is also made here.

(2) *The examination for acid radicals (or anions) in solution.*

(3) *The examination for metal ions (or cations) in solution.*

VIII, 1. PRELIMINARY TESTS

Test (i). Heating in a closed tube.—Place about 0·2 gram of the substance in a dry ignition tube so that none of it remains adhering to the sides and heat cautiously ; the tube should be held in an almost horizontal position. Raise the temperature gradually and carefully note any changes which take place.

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* This additional matter has been introduced at the request of numerous correspondents. It covers the requirements of those that desire a brief introductory course and have only a limited time at their disposal. The abbreviated course will be found suitable for the intermediate and higher school examinations of the various universities and for the ordinary national certificate in chemistry.

Observation	*Inference*
(a) **A gas or vapour is evolved.**	
1. Water is evolved; test with litmus paper.	Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts and hydroxides.
The water is alkaline.	Ammonium salts.
The water is acid.	Readily decomposable salts of strong acids.
2. Oxygen is evolved (rekindles a glowing splint).	Nitrates, chlorates, and certain oxides.
3. Nitrous oxide (rekindles glowing splint) and steam are evolved.	Ammonium nitrate or nitrate mixed with an ammonium salt.
4. Dark brown or reddish fumes (oxides of nitrogen); acidic in reaction.	Nitrates or nitrites of heavy metals.
5. Carbon dioxide is evolved (lime water is rendered turbid).	Carbonates or bicarbonates.
6. Ammonia is evolved (turns red litmus paper blue).	Ammonium salts.
7. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green).	Normal and acid sulphites: thiosulphates; certain sulphates.
8. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black).	Hydrated sulphides or sulphides in the presence of water.
9. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); *very poisonous*.	Unstable chlorides, *e.g.*, of copper; chlorides in the presence of oxidising agents.
10. Bromine is evolved (reddish-brown vapour; choking odour).	Sources similar to chlorine.
11. Iodine is evolved (violet vapours condensing to black crystals).	Free iodine and certain iodides.
(b) **A sublimate is formed.**	
1. White sublimate*.	Ammonium and mercuric salts; As_2O_3; Sb_2O_3.
2. Grey sublimate, easily rubbed to globules.	Hg.
3. Steel-grey sublimate; garlic odour.	As.
4. Yellow sublimate.	S (melts on heating), As_2S_3, HgI_2 (red when rubbed with a glass rod).

* If a white sublimate forms, heat with four times the bulk of anhydrous Na_2CO_3 and a little KCN in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates *Hg* (*Note*: Hg vapour is *very poisonous*); a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates *As*; ammonia evolved (test with mercurous nitrate paper) indicates *ammonium salts*.

Test (ii). Charcoal block reductions.—

(*a*) Heat a little of the substance in a small cavity in a charcoal block in a blowpipe flame.

Observation	*Inference*
1. The substance decrepitates.	Crystalline salts, as NaCl, KCl.
2. The substance deflagrates.	Oxidising agents, *e.g.*, nitrates, nitrites, and chlorates.
3. The substance is infusible or incandescent, or forms an incrustation upon the charcoal.	Apply test (*b*) below.

(*b*) Mix the substance with twice its bulk of anhydrous sodium carbonate, place it in a cavity in a charcoal block, and heat in the reducing flame of the blowpipe.

Observation	*Inference*
1. Incrustation without metal :	
White, yellow when hot.	ZnO.
White, garlic odour.	As_2O_3.
Brown.	CdO.
2. Incrustation with metal :	
White incrustation ; brittle metal.	Sb.
Yellow incrustation ; brittle metal.	Bi.
Yellow incrustation ; grey and soft metal, marks paper.	Pb.
3. Metal without incrustation :	
Grey metallic particles, attracted by magnet.	Fe, Ni, Co.
Malleable beads.	Ag and Sn (white) ; Cu (red flakes).

Test (iii). Flame colourations.—Place a small quantity of the substance on a watch glass, moisten with a little concentrated hydrochloric acid, and introduce a little of the substance on a *clean* platinum wire into the base of the non-luminous Bunsen flame. An alternative method is to dip the platinum wire into concentrated hydrochloric acid contained in a watch glass or test-tube and then into the substance ; sufficient will adhere to the platinum wire for the test to be carried out.

Observation	*Inference*
Persistent golden-yellow flame.	Na.
Violet (lilac) flame (crimson through cobalt-blue glass).	K.
Brick-red (yellowish-red) flame.	Ca.
Crimson flame.	Sr.
Yellowish-green flame	Ba.
Livid-blue flame (wire slowly corroded)	Pb, As, Sb, Bi, Cu.

The sodium flame masks that of other elements, *e.g.*, that of potassium. Mixtures can be readily detected with a direct-vision spectroscope. A less delicate method is to view the flame through two thicknesses of cobalt-blue glass, whereby the yellow colour due to sodium is masked or absorbed; potassium then appears crimson.

Test (iv). Borax bead reactions.—Make a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead in the inner or reducing flame and observe the colour in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, nickel and cobalt; the most characteristic result is for cobalt.

Oxidising Flame	*Reducing Flame*	*Metal*
1. Green when hot; blue when cold.	Colourless or opaque when cold.	Cu.
2. Yellow, hot and cold.	Green, hot and cold.	Fe.
3. Green, hot and cold.	Green, hot and cold.	Cr.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Mn.
5. Blue, hot and cold.	Blue, hot and cold.	Co.
6. Reddish-brown when cold.	Grey when cold.	Ni.

Test (v). Test for the ammonium radical.—Boil about 0·3 gram of the substance with sodium hydroxide solution. The evolution of ammonia, detected by its odour, its action upon litmus paper and upon mercurous nitrate paper, indicates the presence of an *ammonium salt*.

Test (ii). Charcoal block reductions.—

(*a*) Heat a little of the substance in a small cavity in a charcoal block in a blowpipe flame.

Observation	*Inference*
1. The substance decrepitates.	Crystalline salts, as NaCl, KCl.
2. The substance deflagrates.	Oxidising agents, *e.g.*, nitrates, nitrites, and chlorates.
3. The substance is infusible or incandescent, or forms an incrustation upon the charcoal.	Apply test (*b*) below.

(*b*) Mix the substance with twice its bulk of anhydrous sodium carbonate, place it in a cavity in a charcoal block, and heat in the reducing flame of the blowpipe.

Observation	*Inference*
1. Incrustation without metal :	
White, yellow when hot.	ZnO.
White, garlic odour.	As_2O_3.
Brown.	CdO.
2. Incrustation with metal :	
White incrustation ; brittle metal.	Sb.
Yellow incrustation ; brittle metal.	Bi.
Yellow incrustation ; grey and soft metal, marks paper.	Pb.
3. Metal without incrustation :	
Grey metallic particles, attracted by magnet.	Fe, Ni, Co.
Malleable beads.	Ag and Sn (white) ; Cu (red flakes).

Test (iii). Flame colourations.—Place a small quantity of the substance on a watch glass, moisten with a little concentrated hydrochloric acid, and introduce a little of the substance on a *clean* platinum wire into the base of the non-luminous Bunsen flame. An alternative method is to dip the platinum wire into concentrated hydrochloric acid contained in a watch glass or test-tube and then into the substance ; sufficient will adhere to the platinum wire for the test to be carried out.

Observation	*Inference*
Persistent golden-yellow flame.	Na.
Violet (lilac) flame (crimson through cobalt-blue glass).	K.
Brick-red (yellowish-red) flame.	Ca.
Crimson flame.	Sr.
Yellowish-green flame	Ba.
Livid-blue flame (wire slowly corroded)	Pb, As, Sb, Bi, Cu.

The sodium flame masks that of other elements, *e.g.*, that of potassium. Mixtures can be readily detected with a direct-vision spectroscope. A less delicate method is to view the flame through two thicknesses of cobalt-blue glass, whereby the yellow colour due to sodium is masked or absorbed; potassium then appears crimson.

Test (iv). Borax bead reactions.—Make a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead in the inner or reducing flame and observe the colour in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, nickel and cobalt; the most characteristic result is for cobalt.

Oxidising Flame	*Reducing Flame*	*Metal*
1. Green when hot; blue when cold.	Colourless or opaque when cold.	Cu.
2. Yellow, hot and cold.	Green, hot and cold.	Fe.
3. Green, hot and cold.	Green, hot and cold.	Cr.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Mn.
5. Blue, hot and cold.	Blue, hot and cold.	Co.
6. Reddish-brown when cold.	Grey when cold.	Ni.

Test (v). Test for the ammonium radical.—Boil about 0·3 gram of the substance with sodium hydroxide solution. The evolution of ammonia, detected by its odour, its action upon litmus paper and upon mercurous nitrate paper, indicates the presence of an *ammonium salt.*

In order to avoid the necessity of holding the test-paper (litmus, etc.) in the vapour, the following simple device should be used. A test-tube is fitted with a cork carrying a wide tube (at least half the diameter of the test-tube) about 5 cms. long; the bottom of the wide tube should protrude just below the cork (Fig. 46). A test-paper can then be supported in the wide tube by simply folding it slightly over the upper edge of the glass tube. This device is recommended for all reactions in which evolved gases are identified by means of test-papers.

Test (vi). Test for nitrate (or nitrite).—If ammonium is found, continue boiling until ammonia can no longer be detected by its action upon red litmus paper or upon mercurous nitrate paper. Then add a little zinc dust or aluminium powder or finely-powdered Devarda's alloy (Cu, 50%; Al, 45%; Zn, 5%) and warm the mixture gently. Remove the flame as soon as evolution of hydrogen commences and allow the reduction to proceed (the reaction may become vigorous with aluminium powder and cooling with tap water may be necessary to moderate the vigour of the reaction; alternatively, thin aluminium foil may be used). If ammonium is absent, add zinc dust or aluminium powder or Devarda's alloy to the reaction mixture from test (v). If ammonia is evolved, as detected by its action upon red litmus paper or upon filter paper moistened with mercurous nitrate solution, then the presence of *nitrate* or *nitrite* is indicated. The presence of nitrite will generally also be detected in the reaction with dilute sulphuric acid (see test (vii)); if nitrite is absent, then the presence of nitrate alone is established.

It must be emphasised that the mercurous nitrate paper test for ammonia is not applicable in the presence of arsenites. Arsenites are reduced under the above conditions to arsine, which also blackens mercurous nitrate paper.

Test (vii). Action of dilute sulphuric acid.—Treat about 0·3 gram of the substance in a test-tube with a little dilute sulphuric acid and note whether any reaction takes place in the cold (indicated by *C*). Warm gently and observe the effect produced.

Observation	*Inference*
1. Colourless gas is evolved with effervescence; gas is odourless and produces a turbidity when passed into lime water (see Fig. 43). (*C*)	CO_2 from *carbonate.*
2. Nitrous fumes evolved; recognised by reddish-brown colour and odour. (*C*)	NO_2 from *nitrite.*
3. Yellowish-green gas evolved; suffocating odour, reddens then bleaches litmus paper, also turns starch-KI paper blue; *very poisonous.* (*C*)	Cl_2 from *hypochlorite.*
4. Colourless gas evolved with suffocating odour; turns filter paper moistened with $K_2Cr_2O_7$ solution green.	SO_2 from *sulphite.*
5. Colourless gas evolved; gives above tests for SO_2; sulphur is deposited in the solution.	SO_2 and S from *thiosulphate.*
6. Colourless gas evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution.	H_2S from *sulphide**.
7. Odour of vinegar.	$H.C_2H_3O_2$ from *acetate.*
8. Colourless gas is evolved; rekindles glowing splint.	O_2 from *peroxides* of alkali and alkaline earth metals.

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* Many sulphides, especially native ones, are not affected by dilute H_2SO_4; some H_2S is evolved by warming with concentrated HCl alone or with a little tin.

Test (viii). Action of concentrated sulphuric acid.—Treat about 0·3 gram of the substance with 2–3 c.c. of concentrated sulphuric acid and warm the mixture gently, and incline the mouth of the test-tube away from you. (If chlorate is suspected from the preliminary charcoal reduction test to be present, use a very small quantity (less than 0·1 gram) for this test, as a dangerous explosion may result on warming.)

If the substance reacted with dilute sulphuric acid, the addition of concentrated sulphuric acid may result in vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of acid. In such a case, it is best to add dilute sulphuric acid drop-wise (best with a clean dropper) to another portion of the substance until action ceases, and then to add 3–4 c.c. of concentrated sulphuric acid.

The following results may be obtained.

Observation	*Inference*
1. Colourless gas evolved with pungent odour and which fumes in the air; white fumes of NH_4Cl in contact with glass rod wet with NH_4OH solution; Cl_2 evolved on addition of MnO_2 (reddens then bleaches litmus paper).	HCl from *chloride.*
2. Gas evolved with pungent odour, reddish colour, and fumes in moist air; on addition of MnO_2 increased amount of red fumes with odour of Br_2 (fumes colour filter paper moistened with fluorescein solution red).	HBr and Br_2 from *bromide.*
3. Violet vapours evolved, accompanied by pungent acid fumes, and often SO_2 and even H_2S.	HI and I_2 from *iodide.*
4. Pungent acid fumes evolved, often coloured brown by NO_2; colour deepens upon addition of copper turnings (if nitrite absent).	HNO_3 and NO_2 from *nitrate.*
5. Yellow gas evolved in the cold with characteristic odour; explosion or crackling noise on warming *gently* (**DANGER !**).	ClO_2 from *chlorate.*
6. "Oily" appearance of tube in cold; on warming, pungent gas evolved, which corrodes the glass; if moistened glass rod introduced into the vapour, a gelatinous precipitate of hydrated silica is deposited upon it.	HF from *fluoride.*
7. Colourless gas evolved; burns with a blue flame; no charring (*very poisonous*).	CO from *formate.*
8. Colourless gas evolved; renders lime water turbid and also burns with a blue flame; no blackening.	CO and CO_2 from *oxalate.*

VIII, 2. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary tests (vii) and (viii) with dilute sulphuric acid and with concentrated sulphuric acid will have provided useful information as to many acid radicals present. For more detailed information, it is necessary to have a solution containing all (or most) anions free from heavy metals. This is best prepared by boiling the substance with concentrated sodium carbonate solution; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates* of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution. Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur:

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* Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.

$$MA_2 + Na_2CO_3 \rightleftharpoons MCO_3 + 2NaA.$$

The carbonate MCO_3 is insoluble and the sodium salt NaA will pass into solution whether MA_2 is soluble in water or not.

Preparation of solution for testing for anions.—Boil 2 grams of the finely-divided substance or mixture with 25 c.c. of a saturated solution of pure sodium carbonate* (prepared from 4 g. of anhydrous sodium carbonate and 25 c.c. of distilled water) for 10 minutes in a small conical flask with a funnel in the mouth to reduce the loss by evaporation. Filter†, wash the residue with hot distilled water and collect the washings together with the main filtrate; the total volume should be 30–40 c.c. Reject the residue. The sodium carbonate extract will be termed the "*prepared*" solution. Use this solution to carry out the following tests.

1. Sulphate test.—To 3 c.c. of the "prepared" solution add dilute hydrochloric acid until acid (test with litmus paper) and then add 2 c.c. in excess. Boil for 1–2 minutes to expel carbon dioxide completely, and then add about 1 c.c. of barium chloride solution. A white precipitate ($BaSO_4$) shows the presence of *sulphate*. If time permits, confirm by test *1* in Section **IV, 24.**

2. Test for reducing agents.—Acidify 3 c.c. of the "prepared" solution with dilute sulphuric acid and add 1 c.c. of dilute sulphuric acid in excess. Add 3–4 drops of 0·02*N* potassium permanganate solution (prepared by diluting 1 c.c. of 0·1*N* $KMnO_4$ to 5 c.c.) from a dropper. Bleaching of the permanganate indicates the presence of one or more of the following reducing anions: *sulphite, thiosulphate, sulphide, nitrite, bromide, iodide and arsenite.* If the permanganate is not decolourised, heat and observe the result. If the reagent is bleached only on heating, the presence of *oxalate* is indicated. A negative test shows the absence of the above anions.

3. Test for oxidising agents.—Treat 3 c.c. of the "prepared" solution cautiously with 1·5 c.c. of concentrated hydrochloric acid, followed by 3 c.c. of the manganous chloride reagent. A brown (or black) colouration indicates the presence of *nitrate, nitrite, chlorate or chromate.* A negative test indicates the absence of the above oxidising anions except small amounts of nitrates and nitrites. If reducing anions have been found, this test is inconclusive.

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* It is essential to use pure sodium carbonate; the A.R. solid is satisfactory. Some "pure" samples may contain traces of sulphate or chloride: the absence of these impurities should be confirmed by a blank experiment.

† If no precipitate is obtained, the substance is free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required.

Note. The **reagent** consists of a saturated solution of manganous chloride, $MnCl_2,4H_2O$, in concentrated hydrochloric acid. Its action depends upon its conversion by even mild oxidising agents to a dark-brown coloured manganic salt, probably containing the complex $[MnCl_6]^{--}$ or $[MnCl_4]^{--}$ ions.

4. Test with silver nitrate solution.—Acidify 10 c.c. of the "prepared" solution cautiously with dilute nitric acid (use litmus paper). Determine the total volume of the acidified solution with the aid of a measuring cylinder, and add one-

<table>
<tr><td colspan="3">Add 1 c.c. of concentrated HNO_3, followed by $AgNO_3$ solution, slowly and with stirring, until precipitation is complete. (If no ppt. forms, do not add more than 0·5 c.c. of $AgNO_3$ solution.) Filter and wash with very dilute HNO_3 (1 : 20).</td></tr>
<tr><td rowspan="2">Residue.
AgCl white.
AgBr pale yellow.
AgI yellow.</td><td colspan="2">Filtrate. Add a few drops of $AgNO_3$ solution and divide the solution (<i>A</i>) into two unequal parts.
To smaller portion add 1 c.c. of 20% $NaNO_2$ solution (chloride-free). If a white ppt. (AgCl) forms, the presence of chlorate is indicated. If chlorate is present, treat the remainder of solution <i>A</i> with 2 c.c. of $AgNO_3$ solution, 1 c.c. of dilute HNO_3, followed by $NaNO_2$ solution until precipitation is complete. Filter off the AgCl and keep the filtrate <i>B</i>.
To filtrate <i>B</i> (if chlorate is present), or to the larger portion of <i>A</i> (if chlorate is absent), add NaOH solution dropwise (use a dropper) and with vigorous shaking until the solution is just neutral to litmus (1), then add 0·5 c.c. of dilute acetic acid (1 : 2), followed by 1 c.c. of $AgNO_3$ solution, and heat to about 80° (2). If a permanent ppt. forms, add more $AgNO_3$ solution until precipitation is complete. Filter and wash with hot water.</td></tr>
<tr><td>Residue.
Ag_3PO_4 yellow.
Ag_3AsO_4 reddish-brown (3).
$Ag_2C_2O_4$ white.
Ag_2CrO_4 scarlet (4).</td><td>Filtrate.
Reject.</td></tr>
</table>

tenth of the volume of concentrated nitric acid. Boil in a porcelain dish to expel carbon dioxide and other volatile gases* (2–5 minutes); filter, if necessary, and allow to cool. Use the solution to carry out the tests given in the table on p. 495.

Notes. (1) It is essential that the solution be just neutral to litmus or at most barely alkaline; the latter will be indicated by a very slight brown opalescence (due to Ag_2O) obtained after shaking. If much brown silver oxide separates, it will re-dissolve only with difficulty.

(2) Silver acetate is soluble in hot water and is thus held in solution.

(3) Arsenite, if present, will be oxidised by the nitric acid treatment largely to arsenate so that little or no yellow silver arsenite Ag_3AsO_3 will separate here. Arsenite, however, will be readily identified in the analysis for cations by the immediate precipitation of arsenious sulphide As_2S_3 in dilute acid solution. Hence, if no arsenite is found in Group IIB, the presence of arsenate is indicated. It is assumed that the analysis of a mixture of arsenite and arsenate is outside the scope of an elementary course.

(4) If chlorate is present, the sodium nitrite treatment will reduce the chromate (indicated by a yellow or orange solution in *A* or *B*) to green chromic hydroxide, which will precipitate here. In the absence of a chlorate (*i.e.*, when the sodium nitrite treatment has been omitted), scarlet Ag_2CrO_4 is obtained if a chromate is present.

The separations described in the above table are based upon the following facts :—

(i) $AgNO_3$ solution precipitates only AgCl, AgBr and AgI from a dilute nitric acid solution, the other silver salts being soluble.

(ii) $NaNO_2$ solution reduces chlorate to chloride, which is precipitated as AgCl in the presence of $AgNO_3$ solution :

$$NaClO_3 + 3NaNO_2 = NaCl + 3NaNO_3.$$

(iii) In solutions faintly acid with acetic acid, phosphate, arsenate, arsenite, chromate and oxalate are precipitated by $AgNO_3$ solution.

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* If H_2S or SO_2 is evolved, partial oxidation to sulphuric acid will occur. Arsenite, if present, will also be largely oxidised to arsenate, hence no provision for the identification of arsenite is made in the table. Iodide will be partially oxidised by the nitric acid to iodine, which will be readily identified by the brown colour of the solution ; the presence of iodide will also have been indicated in the preliminary test with concentrated sulphuric acid. Bromides are only slightly oxidised to bromine by the nitric acid of the concentration employed (*ca.* $1 \cdot 5N$).

5. Test with calcium chloride solution*.—For this and also for test *6* a "*neutral*" solution is required. This is prepared as follows. Take 5–10 c.c. of the "prepared" solution in a porcelain dish and render faintly acid with dilute nitric acid (use litmus paper). Boil for 3–4 minutes to expel carbon dioxide, allow to cool, then add dilute ammonium hydroxide solution until just alkaline † and boil until neutral. Divide the solution into two equal parts; reserve half for test *6*.

Add $CaCl_2$ solution (equal in volume to that of the solution) and a little dilute acetic acid and allow to stand. A white precipitate indicates the presence of *oxalate* and/or *fluoride*. Filter off the precipitate and dissolve it by pouring a little hot dilute sulphuric acid into the filter. Treat the hot filtrate with a few drops of potassium permanganate solution. If the permanganate is reduced, *oxalate* is present.

6. Test with ferric chloride solution.§—Treat the other portion of the "neutral" solution from *test 5* with aqueous $FeCl_3$ solution.

Reddish-purple colouration indicates *thiosulphate*.

Reddish-brown colouration, yielding a brown precipitate on dilution and boiling, indicates *acetate*.

Yellowish-white precipitate indicates *phosphate*.

Blood-red colouration, discharged by $HgCl_2$ solution, indicates *thiocyanate*.‡

VIII, 3. CONFIRMATORY TESTS FOR ACID RADICALS (ANIONS)

The tests in the preceding section will indicate the acid radicals or anions present. In general, these should be confirmed by at least one distinctive confirmatory test. The following are recommended. Full experimental details will usually be found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (**IV, 2,** *7*) is to be interpreted as Section **IV, 2,** reaction *7*. It is assumed, of course, that interfering acids are absent or have been removed as described below under *Special Tests for Mixtures of Acid Radicals*.

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* Tests *5* and *6* may be omitted by those requiring only a beginner's course in qualitative analysis.

† If a ppt. forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric bases (lead, tin, aluminium and zinc) is indicated. The ppt. should be filtered off and rejected.

§ The bench reagent usually contains excess of free acid added during its preparation in order to produce a clear solution: this may prevent the precipitation of the basic acetate on boiling. It is recommended that Na_2CO_3 or NH_4OH solution be added to 3–4 c.c. of the side-shelf $FeCl_3$ solution until a *slight* permanent precipitate forms; this is filtered off and the filtrate ("neutralised" $FeCl_3$ solution) employed for the test with the "neutral" solution. Alternatively, the slight precipitate may be *just* redissolved by the addition of some of the original $FeCl_3$ solution dropwise.

‡ Thiocyanate is not normally encountered in an elementary course and is given here for the sake of completeness and because of the characteristic nature of the test.

Chloride. Heat solid with concentrated H_2SO_4 and MnO_2; Cl_2 evolved (reddens then bleaches litmus paper and also turns KI-starch paper blue) (**IV, 14,** *2*).

Bromide. Heat solid with concentrated H_2SO_4 and MnO_2; Br_2 evolved (**IV, 15,** *2*) OR chlorine water and CCl_4 test; reddish-brown colouration of CCl_4 layer (**IV, 15,** *5*). The chlorine water may be replaced by acidifying the solution with dilute HCl or dilute H_2SO_4 and adding NaOCl solution.

Iodide. Chlorine water (or NaOCl solution and dilute HCl) and CCl_4 test; violet colouration of CCl_4 layer (**IV, 16,** *4*).

Fluoride. Silicon tetrafluoride test (heat with concentrated H_2SO_4 in a test-tube) (**IV, 17,** *1*); test (viii) in **V, 17**.

Nitrite. Brown ring test with dilute acetic acid or with dilute H_2SO_4 (**IV, 7,** *9*) OR thiourea test (**IV, 7,** *9*).

Nitrate. Brown ring test with concentrated H_2SO_4 (**IV, 18,** *3*), if bromide, iodide and nitrite absent.

Sulphide. Dilute H_2SO_4 on solid, and action of H_2S on lead acetate paper (**IV, 6,** *1*).

Sulphite. Dilute H_2SO_4 on solid, odour of SO_2 and action of SO_2 on $K_2Cr_2O_7$ paper (**IV, 4,** *1*).

Thiosulphate. Dilute H_2SO_4 on solid and liberation of SO_2 ($K_2Cr_2O_7$ paper test) *and* sulphur (**IV, 5,** *1*).

Sulphate. The $BaCl_2$ solution and dilute HCl test is fairly conclusive. Further confirmation is obtained by reduction of the ppt. ($BaSO_4$) on charcoal to sulphide (test for latter with lead acetate solution) (**IV, 24,** *1*).

Carbonate. Action of dilute H_2SO_4 on solid, and lime water test (**IV, 2,** *1*).

Hypochlorite. Action of dilute HCl and test for Cl_2 evolved (**IV, 13,** *4*).

Chlorate. The $AgNO_3$–$NaNO_2$ test (see table) is conclusive.

Chromate. Hydrogen peroxide test with amyl alcohol as organic solvent (**IV, 33,** *4*).

Arsenite. Immediate ppt. of As_2S_3 in dilute HCl solution (**III, 11,** *1*) and absence of ppt. with magnesia mixture (**III, 11,** *3*).

Arsenate. Action of H_2S on acid solution (**III, 12,** *1*), $AgNO_3$ solution test in faintly acetic acid solution (**III, 12,** *2*) and magnesia mixture test (**III, 12,** *3*).

Phosphate. Ammonium molybdate test (temperature not above 40°) (**IV, 28,** *4*).

Acetate. Action of ethyl or of *n*-butyl alcohol and concentrated H_2SO_4 (**IV, 35,** *3*) OR indigo test (**IV, 35,** *9*) using ordinary test-tube or ignition tube.

Oxalate. The $CaCl_2$ test and decolourisation of acidified $KMnO_4$ solution at about 70° is sufficiently conclusive.

VIII, 4. SPECIAL TESTS FOR MIXTURES OF ACID RADICALS*

1. **Carbonate in the presence of Sulphite.**—Sulphites, on treatment with dilute sulphuric acid, liberate sulphur dioxide which, like carbon dioxide, produces a turbidity with lime water. The dichromate test for sulphites is, however, not influenced by the presence of carbonates. To detect carbonates in the presence of sulphites, treat the solid mixture with dilute sulphuric acid and pass the evolved gases through a small wash-bottle or boiling tube containing potassium dichromate solution and dilute sulphuric acid. The solution will be turned green and the sulphur dioxide will, at the same time, be completely removed; the residual gas is then tested with lime water in the usual manner.

An alternative procedure is to add a little powdered potassium dichromate to the mixture and then to warm with dilute sulphuric acid: the evolved gas is then passed through lime water.

The above method can, of course, be applied in the presence of thiosulphates.

2. **Nitrate in the presence of Nitrite.**—The nitrite is readily identified in the presence of a nitrate by treatment with dilute mineral acid, potassium iodide and starch paste (or potassium iodide-starch paper) or by means of the thiourea test. The nitrate cannot, however, be detected in the presence of nitrite since the latter gives the brown ring test with ferrous sulphate solution and *dilute* sulphuric acid. The nitrite is therefore completely decomposed first by one of the following methods:—

(i) boil with ammonium chloride solution until effervescence ceases†;

(ii) warm with urea and dilute sulphuric acid until evolution of gas ceases†;

(iii) add the solution to solid hydrazine sulphate; reaction takes place in the cold and the danger of slight oxidation of nitrite to nitrate is considerably reduced.

$$N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O;$$
$$N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O.$$

The brown ring test for nitrate can then be applied.

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* Full experimental details of the various tests will be found in Chapter IV.

† *Traces* of nitrate are always formed in this reaction.

3. **Nitrate in the presence of Bromide and Iodide.**—The brown ring test for nitrates cannot be applied in the presence of bromides and iodides since the liberation of free halogen with concentrated sulphuric acid will obscure the brown ring due to the nitrate. The solution is therefore boiled with sodium hydroxide solution until ammonium salts, if present, are completely decomposed, and the solution is then cooled under the tap. Powdered Devarda's alloy or aluminium powder or zinc dust is then added and the mixture *gently* warmed. The evolution of ammonia, detected by its smell, its action upon red litmus paper and upon mercurous nitrate paper (see Section **III, 36,** reaction *1*) indicates the presence of a nitrate.

An alternative method is to remove the halides by precipitation with an almost saturated solution of silver sulphate (nitrate-free) and any excess of the latter with sodium carbonate solution ; the nitrate is then tested for in the filtrate in the usual way.

4. **Nitrate in the presence of Chlorate.**—The chlorate interferes with the brown ring test (compare Section **IV, 19,** reaction *1*). The nitrate is reduced to ammonia as described under *3* ; the chlorate is at the same time reduced to chloride which may be tested for with silver nitrate solution and dilute nitric acid.

If a chloride is originally present, it may be removed first by the addition of saturated silver sulphate solution.

5. **Chloride in the presence of Bromide and Iodide.**—This procedure involves the removal of the bromide and iodide with potassium or ammonium persulphate in the presence of dilute sulphuric acid. The free halogens are thus liberated, and may be removed either by simple evaporation (addition of water may be necessary to maintain the original volume) or by evaporation at about 80° in a stream of air.

$$K_2S_2O_8 + 2KI = I_2 + 2K_2SO_4 ;$$
$$K_2S_2O_8 + 2KBr + 2H_2SO_4 = Br_2 + 4KHSO_4.$$

Add solid potassium or ammonium persulphate to the " prepared " solution of the mixed halides contained in a conical flask ; strongly acidify with dilute sulphuric acid ; heat the flask to about 80°, and aspirate a current of air through the solution with the aid of a filter pump (see Fig. 44 in Section **IV, 44,** *5*) until the solution is colourless. Add more solid persulphate or water as may be found necessary. Test the residual colourless liquid for chloride with silver nitrate solution and dilute nitric acid.

6. **Chloride in the presence of Iodide (Bromide being absent).**—Add excess of silver nitrate solution to the " prepared " solution acidified with dilute nitric acid, and filter; reject the filtrate. Wash the precipitate with dilute ammonium hydroxide solution and filter again. Add dilute nitric acid to the washings; a white precipitate of silver chloride indicates the presence of chloride.

The separation is based upon the solubility of silver chloride in dilute ammonium hydroxide solution and the practical insolubility of silver iodide in this reagent.

7. **Chloride in the presence of Bromide (Iodide being absent).**—Acidify the " prepared " solution with dilute nitric acid and add an equal volume of concentrated nitric acid. Boil for 5 minutes or until all the bromine is expelled; then add silver nitrate solution. A white precipitate indicates chloride present.

8. **Bromide and Iodide in the presence of one another.**—The presence of a chloride does not interfere with the reactions described below. Acidify the " prepared " solution with dilute sulphuric acid and add 1–2 c.c. of carbon tetrachloride; add 1–2 drops of dilute sodium hypochlorite solution* (best with a dropper) and shake; a violet colouration in the carbon tetrachloride layer indicates iodide. Continue the addition of the hypochlorite solution *drop by drop* to oxidise the iodine to iodate (colourless) and shake after each addition. The violet colour will disappear, and a reddish-brown colouration of the carbon tetrachloride layer, due to dissolved bromine, will be obtained if a bromide is present. If iodide alone is present, the solution will be colourless after the violet colour has disappeared.

9. **Phosphate in the presence of Arsenate.**—Both arsenate and phosphate give a yellow precipitate on warming with ammonium molybdate solution and nitric acid, the latter on gentle warming (not above 40°) and the former on boiling. Also both anions give a white precipitate with magnesia

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* The use of dilute sodium hypochlorite solution and dilute acid is far more satisfactory than chlorine water. Alternatively, a solution of chloramine-T (15 grams per litre) may be employed; this is a source of hypochlorous acid (and therefore of chlorine):

$$CH_3.C_6H_4.SO_2NClNa + H_2O \rightleftharpoons CH_3.C_6H_4.SO_2NH_2 + NaOCl.$$

mixture. It must also be remembered in connexion with the precipitation of Group II that arsenates are only slowly precipitated by hydrogen sulphide in dilute acid solution.

Acidify the " prepared " solution with dilute hydrochloric acid, pass in sulphur dioxide to reduce the arsenate to arsenite, boil off the excess of sulphur dioxide (test with potassium dichromate paper), and pass hydrogen sulphide into the solution to precipitate the arsenic as arsenious sulphide: continue the passage of hydrogen sulphide until no more precipitate forms. Filter, boil off the hydrogen sulphide, and test the filtrate for phosphate by the ammonium molybdate test or with magnesia mixture.

An alternative method for the elimination of arsenate is the following. Acidify the " prepared " solution with dilute hydrochloric acid and then add one quarter of the volume of concentrated hydrochloric acid (the total volume should be about 20 c.c.). Add 1 c.c. of 5 per cent. potassium iodide solution, heat to boiling, and pass hydrogen sulphide into the boiling solution until precipitation is complete (5–10 minutes). Filter off the arsenious sulphide, and boil off the hydrogen sulphide from the filtrate. Add ammonium hydroxide solution until alkaline and excess of magnesia mixture. A white precipitate indicates the presence of phosphate.

$$As_2O_5 + 4HI \rightleftharpoons As_2O_3 + 2H_2O + 2I_2 ;$$
$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O ;$$
$$2I_2 + 2H_2S \rightleftharpoons 4HI + 2S.$$

VIII, 5. EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

Preparation of a solution of the solid.—Since the whole scheme for the analysis of cations depends upon the reactions of ions, it is clear that it is first necessary to get the substance into solution. Water is first tried in the cold and then on warming. If insoluble in water, the following reagents are tried as solvents in the order indicated: dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid, concentrated nitric acid, and *aqua regia* (3 volumes of concentrated HCl to 1 volume of concentrated HNO_3). Most substances encountered in an elementary course will dissolve in either water or dilute hydrochloric acid. If concentrated hydrochloric acid has to be used, the solution must be considerably diluted before proceeding with the analysis, otherwise certain cations, such as cadmium and lead, will not be precipitated by hydrogen sulphide. When concentrated nitric acid or *aqua regia* is employed as the solvent, the solution must be evaporated almost to dryness, a little hydrochloric acid added, the solution evaporated again to small bulk, and then diluted with water to dissolve the soluble nitrates (or chlorides). This evaporation is necessary because the nitric acid may react with the hydrogen sulphide subsequently employed in the Group analysis.

To discover the most suitable solvent, treat portions of 0·2 gram* of the finely-powdered substance successively with 3–4 c.c. of (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid, and (6) *aqua regia* in the order given. Try the solubility first in the cold and then on warming; if in doubt whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass. If the substance dissolves in water, proceed immediately to the test for the metal ions. If the use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I; the precipitate may either be filtered off and examined for this Group, or else the original substance may be dissolved in dilute nitric acid. If concentrated acids are employed for dissolution, the remarks in the previous paragraph must be borne in mind.

When a suitable solvent has been found, the solution for analysis is prepared with 0·5–1·0 gram of the solid; the volume of the final solution should be 15–20 c.c.

The subsequent analysis for cations is described in Section **V, 5** (**B**) and is based on the general separation Table XXVI; it need not be further discussed here. Attention is, however, drawn to the necessity for the adjustment of the acidity before precipitating with hydrogen sulphide (see Note *2* to Table XXVI) and to the experimental details for precipitation (see Note *2* to Table XXIV). If desired, the tube attached to the source of hydrogen sulphide (see Fig. 11 (*c*) in Section **II, 2**) may be shorter and extend to just below the stopper; this has the advantage that no precipitate deposits on the delivery tube, but the latter must nevertheless be thoroughly washed with distilled water after each precipitation. The procedure would then be as follows. Pour the solution into the flask and insert the stopper tightly into the neck. Connect to the source of hydrogen sulphide through a wash-bottle containing water, open the screw clip and allow a current of the gas to bubble through the wash-bottle into the flask for about one minute; the air over the solution is thus displaced by hydrogen sulphide. Close the screw clip tightly, then *slowly* shake the flask with a *gentle* swirling movement: do not splash the liquid into the neck of the flask. A rapid stream of hydrogen sulphide will pass through the wash-bottle into the conical flask as precipitation of the sulphide proceeds. Precipitation will be complete and the solution saturated with hydrogen sulphide when the bubbling either stops altogether or is reduced to 1–2 bubbles a minute (usually after 2–5 minutes). When saturation is complete, turn off the stop-cock on the source of hydrogen sulphide and then disconnect the flask.

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* This is most simply estimated by weighing out 1 gram and dividing it into 5 approximately equal parts.

The use of an open test-tube for saturation with hydrogen sulphide is very wasteful and is not recommended.

Oxides, Hydroxides, Free Metals, and Simple Alloys.—If a solid substance is found to contain no anions, it may be an oxide, or hydroxide, or a metal or a mixture of metals, or an alloy. Metals and alloys have certain characteristic physical properties; many metals evolve hydrogen on treatment with dilute acids. As a rule, nitric acid must be employed as solvent, and it will then be necessary to remove the excess of nitric acid (as already described above) before proceeding to the Group analysis.

VIII, 6. ANALYSIS OF A LIQUID

If a liquid is supplied for analysis, proceed as follows :—

(1) Observe the colour, odour and any special physical properties.

(2) Test its reaction towards litmus paper.

(*a*) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.

(*b*) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, sulphides, hypochlorites and peroxides of the alkali metals, *etc.*

(*c*) *The solution reacts acid* : this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to a solution of salts in acids.

(3) Evaporate a portion of the liquid to dryness on the water bath (use a porcelain dish and stand it on a beaker half filled with water, the latter being heated by a Bunsen burner) ; carefully smell vapours evolved from time to time. If a solid residue remains, examine as detailed above for a solid substance. If a liquid remains, evaporate cautiously on a wire gauze in the fume cupboard ; a solid residue should then be examined in the usual way. If no residue remains, then the liquid consists of some volatile substance which may be water or water containing certain gases or volatile substances, such as CO_2, NH_3, SO_2, H_2S, HCl, HBr, HI, H_2O_2 or $(NH_4)_2CO_3$, all of which can be readily detected by special tests. It is best to neutralise with sodium carbonate and test for acid radicals (anions).

Droppers.—These are the so-called " medicine droppers " and suitable types may be purchased. They are very useful for adding small volumes of reagents (particularly drop-wise) and also for washing precipitates. If calibrated, say at 1 c.c. intervals, droppers may be used for measuring small volumes.

Droppers are inexpensive, but they can be readily made by the student. Draw out a length of glass tubing (about 20 cms. long and of about 7 mm. diameter) in the centre by suitably heating in a flame ; cut the tube in the middle of the drawn-out portion and thus obtain two jets. Heat the wider end and enlarge it with the aid of a file so that it will securely hold a rubber teat. The teat should be of such size that liquid cannot be drawn into it. The dropper may be calibrated by holding it vertically and allowing distilled water to flow dropwise into a small measuring cylinder ; 1 c.c. intervals should be marked by means of a file. The number of drops (preferably about 25) per c.c. should also be determined.

The rubber teat should be removed and the glass tube thoroughly rinsed with distilled water immediately after use.

VIII, 7. COURSE OF INSTRUCTION FOR ABBREVIATED ELEMENTARY COURSE

For further details the student is referred to Section **A, 4.** Only the reactions of the cations and anions are given here.

The student should pay particular attention to (1) the exact experimental conditions of the reaction; (2) the colour and physical characteristics (*e.g.*, whether crystalline, amorphous or gelatinous) of each precipitate; and (3) the solubility of each precipitate in excess of the precipitant, or in solutions of other reagents. He should, as far as possible, represent the chemical reactions by equations, and then check his own equations against those given in the text. This will provide excellent practice in writing and balancing equations, and also help to impress the reactions upon his memory.

REACTIONS OF THE CATIONS

Pb^{++}. Section **III, 2,** reactions *1, 3, 4*; blowpipe test.
Hg_2^{++}. Section **III, 3,** reactions *1, 4, 6, 7.*
Ag^+. Section **III, 4,** reaction *1*; blowpipe test.

Identification of a metal in the solution supplied by the teacher by means of Table XVII (Section **III, 5**).

Hg^{++}. Section **III, 6,** reactions *1, 2*; dry test.
Bi^{+++}. Section **III, 7,** reactions *1, 3, 5, 6.*
Cu^{++}. Section **III, 8,** reactions *1, 2, 3, 4, 5, 8.*
Cd^{++}. Section **III, 9,** reactions *1, 3, 4.*

Identification of a metal or metals in the solution supplied by means of Table XVIII (Section **III, 10**).

As (ous). Section **III, 11,** reactions *1, 2, 3.*
As (ic). Section **III, 12,** reactions *1, 2, 3, 4.*
Sb (ous). Section **III, 14,** reactions *1, 2, 5, 8.*
Sn^{++}. Section **III, 16,** reactions *1, 2, 3.*
Sn^{++++}. Section **III, 17,** reactions *1, 3, 4.*

Identification of a metal or metals in the solution supplied by means of Table XIX (Section **III, 18**).

Fe^{++}. Section **III, 19,** reactions *1, 2, 3, 4, 6, 7, 8.*
Fe^{+++}. Section **III, 20,** reactions *1, 2, 3, 4, 5, 6, 10.*
Al^{+++}. Section **III, 21,** reactions *1, 2, 3, 7*; dry test.
Cr^{+++}. Section **III, 22,** reactions *1, 2, 3, 6*; dry test (iii).

Identification of a metal or metals in the solution supplied by means of Table XX (Section **III, 23**).

Co^{++}. Section **III, 24,** reactions *1, 2, 3, 5, 6, 7*; dry test (ii).
Ni^{++}. Section **III, 25,** reactions *1, 2, 3, 6, 7, 8*; dry test (ii).
Mn^{++}. Section **III, 26,** reactions *1, 2, 3, 5, 7*; dry test (ii).
Zn^{++}. Section **III, 27,** reactions *1, 2, 3*; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXI (Section **III, 28**).

Ba^{++}. Section **III, 29,** reactions *1, 2, 3, 4, 6*; dry test.
Sr^{++}. Section **III, 30,** reactions *1, 2, 3, 4, 5, 6*; dry test.
Ca^{++}. Section **III, 31,** reactions *1, 2, 3, 4, 5, 6, 7*; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXII (Section **III, 32**).

Mg^{++}. Section **III, 33,** reactions *1, 2, 3, 5, 8*; dry test.
K^{+}. Section **III, 34,** reaction *1*; dry test.
Na^{+}. Section **III, 35,** reaction *1*; dry test.
NH_4^{+}. Section **III, 36,** reaction *1*; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXIII (Section **III, 38**).

REACTIONS OF THE ANIONS

CO_3^{--}. Section **IV, 2,** reactions *1, 2*.
HCO_3^{-}. Section **IV, 3,** reactions (i), (ii), (iii).
SO_3^{--}. Section **IV, 4,** reactions *1, 2, 4, 5, 9*.
$S_2O_3^{--}$. Section **IV, 5,** reactions *1, 2, 4, 8*.
S^{--}. Section **IV, 6,** reactions *1, 2, 3, 4*.
NO_2^{-}. Section **IV, 7,** reactions *1, 2, 7, 8, 9*.
Cl^{-}. Section **IV, 14,** reactions *1, 2, 3*.
Br^{-}. Section **IV, 15,** reactions *1, 2, 3, 5*.
I^{-}. Section **IV, 16,** reactions *1, 2, 4*.
F^{-}. Section **IV, 17,** reactions *1, 2*.
NO_3^{-}. Section **IV, 18,** reactions *1, 2, 3, 4*.
ClO_3^{-}. Section **IV, 19,** reactions *1, 2, 4, 10*.
SO_4^{-}. Section **IV, 24,** reaction *1*.
PO_4^{---}. Section **IV, 28,** reactions *1, 3, 4, 5*.
CrO_4^{--}. Section **IV, 33,** reactions *1, 2, 4, 6*.
$C_2H_3O_2^{-}$ (acetate). Section **IV, 35,** reactions *1, 2, 3, 6, 9*.
$C_2O_4^{--}$ (oxalate). Section **IV, 37,** reactions *1, 2, 3, 4*.

CHAPTER IX

SEMIMICRO QUALITATIVE ANALYSIS

In **macro analysis** described in Chapters V and VIII, the quantity of total substance employed was 0·5–1 gram and the volume of the solution taken for the analysis of cations was about 20 c.c. In what is usually termed **semimicro analysis** the quantity used for the analysis is reduced by a factor of 0·1–0·05, *i.e.*, to about 50 mg. in 1 c.c. For **micro analysis** the factor is of the order of 0·01 or less. There is, however, no sharp line of demarcation between semimicro and micro analysis. It will be observed that only the scale of the operations has been reduced; the concentrations of the ions remain unchanged. An introduction to the experimental technique of micro analysis was given in Section **II, 3.** The technique of semimicro work will now be described.

IX, 1. EXPERIMENTAL TECHNIQUE OF SEMIMICRO ANALYSIS

The essential technique of semimicro analysis does not differ very greatly from that of macro analysis. Since volumes of the order of 1 c.c. are dealt with, the scale of the apparatus

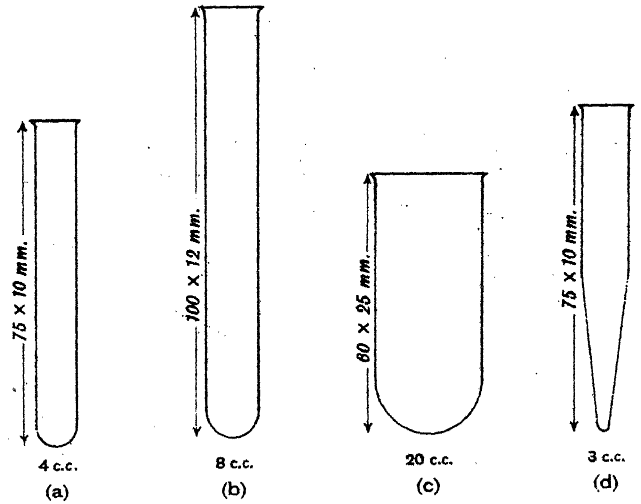

Fig. 49.

is reduced, but it may be said at once that as soon as the simple technique has been acquired and mastered, the student will find it just as easy to manipulate these small volumes and quantities as to work with larger volumes and quantities in ordinary test-tubes (150 × 20 mm.) and related apparatus. Particular care must be directed to having both the apparatus and the working bench scrupulously clean.

Test tubes and centrifuge tubes. Small test-tubes (either 100 × 12 mm. or 75 × 10 mm.) are used for reactions which do not require boiling. Where a precipitate is to be separated by centrifuging, a test-tube with a tapered bottom, known as a **centrifuge tube** (Fig. 49 *d*), is usually employed; here, also, the contents cannot be boiled as "bumping" will occur. Various sizes are available, but the 3 c.c. centrifuge tube is the most widely used. For rapid concentration of a solution by means of a free flame, the **semimicro boiling tube** (60 × 25 mm.; Fig. 49 *c*) is recommended.

Stirring rods. Solutions do not mix readily in semimicro test-tubes and centrifuge tubes; mixing is best effected by the use of stirring rods. Two types are shown in Fig. 50. The first can be readily prepared by heating a length of solid glass rod near the middle until the glass softens, pushing the glass together to thicken it slightly, and when the thickened portion is thoroughly soft, withdrawing from the flame, and slowly pulling out the softened portion to a diameter of 2–3 mm. When cold, the 2–3 mm. glass rod is cut up into lengths of about 12 cm. The sharp edges are fire-polished by heating momentarily in a flame. A handle may be formed, as in Fig. 50 (*b*), by heating about 1 cm. from the end and bending it back to an angle of 45°.

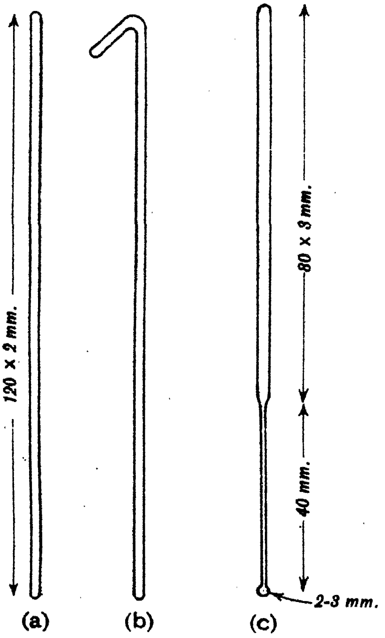

Fig. 50.

A platinum wire may sometimes be used for stirring.

Droppers. Reagents. For handling liquids in semimicro analysis, a *dropper* * is generally employed. Two varieties are shown in Fig. 51 *a* and *b*: the former is usually employed with 30 c.c. (1 ounce) reagent bottles (hence this will be termed a *reagent dropper*), whilst the latter, the capillary of which is long enough to reach to the bottom of a semimicro test-tube or 3 c.c. centrifuge tube, finds application for removing supernatant liquids from test- and centrifuge-tubes and for the semimicro quantitative addition of reagents. Dropper (*b*) will be called a *capillary dropper*.

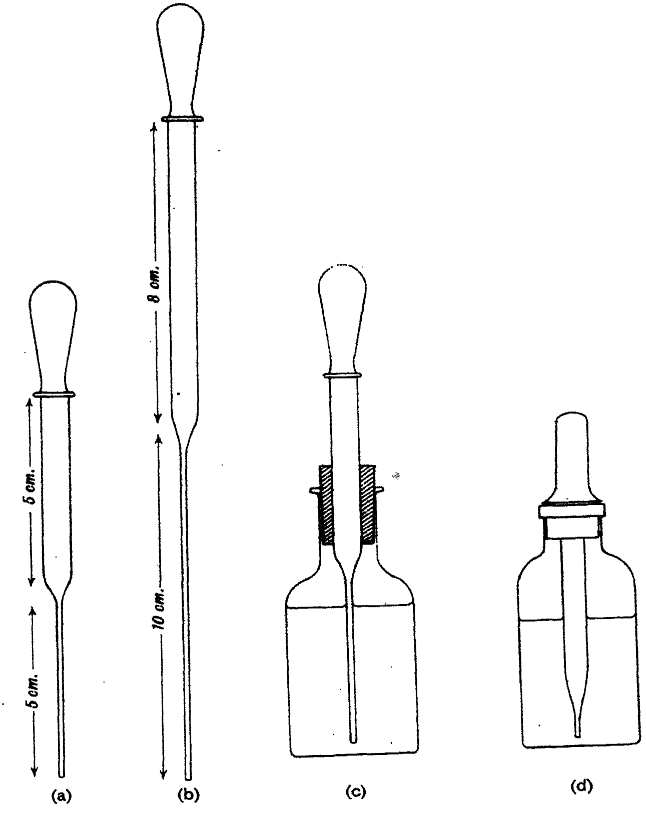

Fig. 51.

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* Also termed medicine dropper, dropper pipette, capillary dropper, and capillary pipette.

Whilst both types of dropper may be purchased, it is quite a simple operation (and excellent practice) to make them from glass tubing. To make a capillary dropper, take a piece of glass tubing about 20 cm. long and of 7 mm. bore and heat it near the middle in a Bunsen or blowpipe flame, rotating slowly all the time. When the centre is soft, allow the glass to thicken *slightly* by continuing the heating and rotating whilst exerting a gentle inward pressure from the ends. Remove the tube from the flame and *slowly* draw out the softened portion to form a fairly thick-walled capillary about 20 cm. long and 2 mm. diameter. When cold, cut the capillary at the mid-point with a file. Fire-polish the capillary ends by rotating in a flame for a moment or two. In order that a rubber bulb (teat) may fit securely on the wide end, heat it cautiously in a flame until just soft, and whilst rotating slowly open it up with a file or glass-worker's triangular " reamer " ; alternatively, the softened end of the tube may be quickly pressed down on an asbestos or uralite sheet or upon some other inert surface. A reagent dropper is made in a similar manner except that it is unnecessary to appreciably thicken the middle of the tube before drawing out.

Before use the droppers must be calibrated, *i.e.*, the volume of the drop delivered must be known. Introduce some distilled water into the dropper by dipping the capillary end into some distilled water in a beaker and compressing and then releasing the rubber teat or bulb. Hold the dropper *vertically* over a clean dry 5 c.c. measuring cylinder, and gently press the rubber bulb. Count the number of drops until the meniscus reaches the 2 c.c. mark. Repeat the calibration until two results are obtained which do not differ by more than 2 drops. Calculate the volume of a single drop. The dropper should deliver between 30 and 40 drops per c.c. Attach a small label to the upper part of the dropper giving the number of drops per c.c.

A *semimicro reagent bottle* may be easily constructed by inserting a reagent dropper through a cork or rubber stopper that fits a 30 c.c. (1 ounce) bottle—Fig. 51, *c*.* One ounce dropping bottles, Fig. 51, *d*, may be purchased ; the Barnes dropping bottle is inexpensive and quite suitable. For concentrated acids and other highly corrosive liquids, dropping bottles cannot be used because of their action upon the rubber, 30 c.c. glass-stoppered bottles are satisfactory containers ; these reagents are handled with droppers, which are thoroughly washed with distilled water immediately after use. Great care must be taken to prevent the reagent from entering the rubber teat of the dropper : this is ensured by depressing the rubber teat only *slightly* before introducing the tip of the dropper into the reagent.

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* Sixty c.c. bottles may be employed, if desired.

Each student should be provided with a solid wooden stand housing the following reagents in 30 c.c. reagent bottles.

Reagent Bottles Fitted with Reagent Droppers

Hydrochloric acid, dil.	$5N$	Ammonium sulphide	$6N$
Sulphuric acid, dil.	$5N$	Silver nitrate	$0{\cdot}1N$
Nitric acid, dil.	$5N$	Barium chloride	$0{\cdot}5N$
Acetic acid, dil.	$5N$	Ferric chloride	$0{\cdot}5N$
Sodium hydroxide, dil.	$5N$	Hydrogen peroxide	(" 10 volume ") *
Ammonium hydroxide, dil.	$5N$	Sodium hypochlorite	(10%) *
Ammonium hydroxide, conc.	$15N$	Potassium ferrocyanide	$0{\cdot}5N$
Potassium chromate	$0{\cdot}5N$	Lime water	$0{\cdot}04N$
Ammonium carbonate	$4N$	Sodium phosphate	N

Glass-Stoppered Bottles

Hydrochloric acid, conc.	$12N$	Sulphuric acid, conc.	$36N$
Nitric acid, conc.	$16N$	Manganous chloride reagent	

Solid Reagents

Sodium carbonate (anhydrous)	Ammonium chloride
Ferrous sulphate	Borax

Filtration. The filter paper-funnel method of separating a solid suspended in a liquid is largely replaced by that employing a **centrifuge**. The advantages of the latter are: (i) speed, (ii) the precipitate is concentrated into a small volume so that small precipitates are readily observed and their relative magnitudes estimated, and (iii) concentrated acids, alkalis and other corrosive liquids can be easily manipulated.

The centrifuge. The theory of this instrument is given below.

The rate of settling r_s (cm./sec.) of spherical particles of density d_p and of radius a (cm.) in a medium of viscosity η (c.g.s. units) and of density d_m is given by Stokes' law :

$$\frac{2a^2g(d_p - d_m)}{9\eta} \tag{1}$$

where g is the acceleration due to gravity (981 cm./sec.^{2}). It is evident from the equation that the rate of settling is increased by : (*a*) an increase in the size of the particles a ; (*b*) an increase in difference between the density of the particles d_p and that of the medium d_m ; (*c*) a decrease in the viscosity η of the medium ; and (*d*) an increase in the acceleration due to gravity g. Fine crystalline particles tend to increase in size when allowed to stand in the liquid in which they are precipitated, particularly when the solution is maintained at elevated temperatures and shaken occasionally. The coagulation of colloidal and gelatinous precipitates is also accelerated by high temperatures and stirring, and also by the addition of certain electrolytes. Moreover, an increase in temperature reduces the viscosity and also increases the difference $(d_p - d_m)$. This explains why centrifuge tubes or test-tubes in which precipitates are formed are usually placed in a hot water bath and shaken from time to time before separation of the mother liquor. The effect of these factors is, however, comparatively small. To really accelerate the rate of settling, the force on the particle g (acceleration due to gravity) must be changed. This is readily and conveniently achieved with the aid of a centrifuge.

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* Amber-coloured bottles.

The relative rates of settling in a centrifuge tube and in a stationary test-tube may be derived as follows. The centrifugal force F_c upon a particle of effective mass m (grams) moving in a circle of diameter r (cm.) at n revolutions per second is given by:

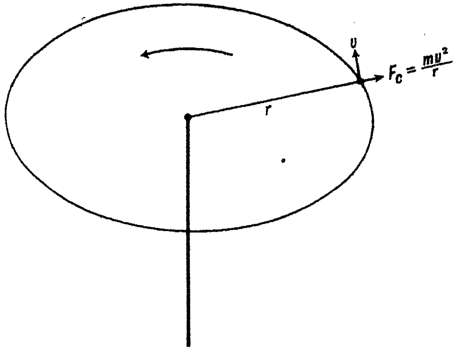


Fig. 52.

$$F_c = ma = \frac{mv^2}{r} = \frac{m(2\pi rn)^2}{r} = m.4\pi^2rn^2,$$

where a is the acceleration (cm./sec.^{2}), v is the velocity (cm./sec.), and $\pi = 3{\cdot}1416$. The gravitational force F_g on a particle of mass m is given by:

$$F_g = m.g$$

$$\frac{F_c}{F_g} = \frac{m.4\pi^2rn^2}{mg} = \frac{4\pi^2rn^2}{g}$$

Expressing rotations per second n in rotations per minute N, and substituting for π, we have:

$$\frac{F_c}{F_g} = \frac{4\pi^2rN^2}{981 \times 60^2} = 1{\cdot}118 \times 10^{-5}\,rN^2 \qquad (2)$$

Thus a centrifuge with a radius of 10 cm. and a speed of 2000 revolutions per minute has a comparative centrifugal force of $1{\cdot}118 \times 10^{-5} \times 10 \times (2000)^2 = 447$, say, 450 times the force of gravity. A precipitate which settles in, say, 10 minutes by the force of gravity alone will settle in 10 × 60/450 or in 1·3 seconds in such a centrifuge. The great advantage of a centrifuge is thus manifest.

Several types of centrifuge are available. The most inexpensive kind is a small 2-tube hand centrifuge with protecting bowl and cover (Fig. 53, A); if properly constructed this will give speeds up to 3,000 r.p.m., with 3 c.c. centrifuge tubes.* In using a centrifuge the following points should be borne in mind:

(1) The two tubes should have approximately the same size and weight.

(2) The tube should not be filled beyond 1 cm. from the top.

(3) Before centrifuging a precipitate contained in a centrifuge tube, prepare the balancing tube by adding sufficient distilled water from a dropper to an empty tube of the same size until the liquid levels in both tubes are approximately the same.

(4) Insert the tubes in diametrically opposite positions in the centrifuge; the head will thus be balanced and vibration will be reduced to a minimum. Fix the cover in place.

(5) Start the centrifuge slowly and smoothly, and bring it to the maximum speed within a few turns of the handle. Maintain the maximum speed for about 30 seconds, and then allow the centrifuge to come to rest of its own accord by releasing the handle. A little practice will allow one to judge

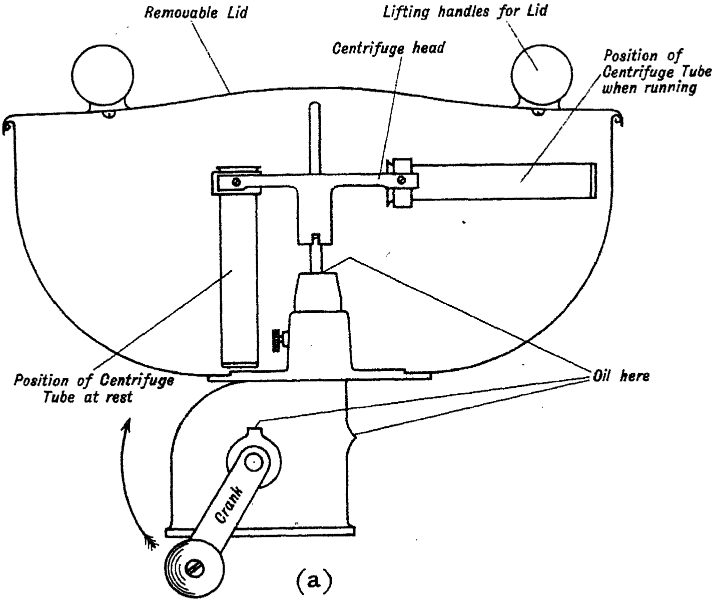
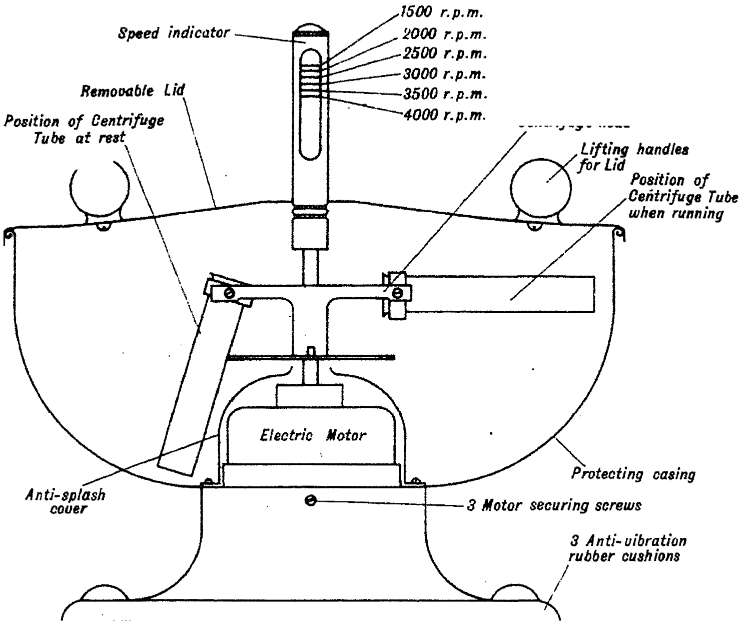

Removable Lid
Lifting handles for Lid
Centrifuge head
Position of Centrifuge Tube when running
Position of Centrifuge Tube at rest
Oil here
Crank
(a)

Fig. 53A.

* See footnote on p. 490.

the exact time required to pack the precipitate tightly at the bottom of the tube. It is of the utmost importance to avoid sudden strains or vibrations as these may result in stirring up the mixture and may be damaging to the apparatus.



(b)

Fig. 53B.

Electrically-driven centrifuges (Fig. 53,B) * are marketed, but are more expensive. In the author's view, a well-made hand semimicro centrifuge is highly satisfactory for students' use, and it is doubtful whether the additional outlay for an " electric centrifuge " is really necessary for instructional courses. The speed of an electrically-driven centrifuge can usually be controlled and reaches a maximum of about

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* Excellent semimicro centrifuges, both hand and electrical, are manufactured by Moseley Centrifuge and Engineering Co., 119 Copenhagen Street, London, N. 1, and are illustrated in Fig. 53 and in Fig. 70. The electrical centrifuge made by the International Equipment Co., of Boston, Mass., U.S.A., is highly satisfactory for semimicro work and is recommended. An inexpensive centrifuge with an angle safety head (the so-called *angle centrifuge*) is marketed as a " Waco separator " by Wilkens-Anderson Co., of 111 N. Canal Street, Chicago, U.S.A.; this Firm has an excellent selection of semimicro apparatus.

4,000 r.p.m. The instructions for use are similar to those given above for hand centrifuges with the addition of the following :—

(6) Switch the current on with the resistance fully in circuit; gradually move the resistance slider over until the necessary speed is attained. After 30 seconds, move the slider back to the original position (make certain that the current is switched off). Allow 30 seconds for the centrifuge to come to rest, raise the lid, and remove the tubes.

(7) Never leave the centrifuge whilst it is in motion.

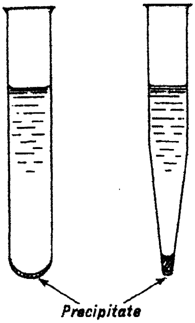


Fig. 54.

Most semimicro centrifuges will accommodate both semimicro test-tubes (75 × 10 mm.) and centrifuge tubes (up to 5 c.c. capacity). The advantages of the latter include (*a*) easier removal of the mother liquor with a dropper, and (*b*) with small quantities of solids, the precipitate is more clearly visible (and the relative quantity is therefore more easily estimated) in a centrifuge tube (Fig. 54).

To remove the supernatant liquid, a capillary dropper is generally used. The centrifuge tube is held at an angle in the left hand, the rubber teat or nipple of the capillary dropper, held in the right hand, is compressed to expel the air and the capillary end is lowered into the tube until it is just below the liquid (Fig. 55). As the pressure is *very slowly* released the liquid rises in the dropper and the latter is lowered further into the liquid until all the liquid is removed. Great care should be taken as the capillary approaches the bottom of the centrifuge tube that the tip does not touch the precipitate. The solution in the dropper should be perfectly clear: it can be transferred to another vessel by merely compressing the rubber bulb. In difficult cases, a little cotton wool may be

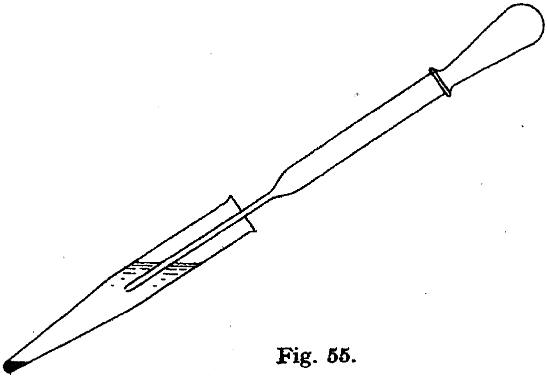
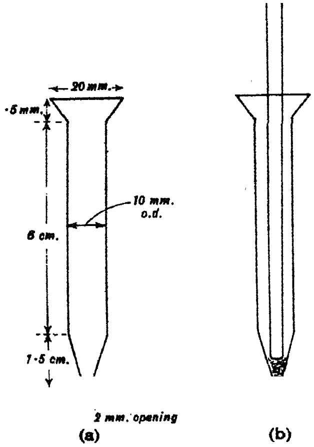


Fig. 55.

inserted in the tip of the dropper and allowed to protrude about 2 mm. below the glass tip; any excess of cotton wool should be cut off with scissors.

The pressure-filter tube method. Where a centrifuge is not available (or for those cases where the density of the solid does not differ appreciably from that of the liquid and the rate of settling is therefore slow—see equation *1*, p.487)—another technique, which dispenses with the use of filter paper, may be adopted for the separation of solid from the accompanying liquid. This is the pressure-filter tube method of H. H. Barber (1940). A special tube, termed a *pressure-filter tube* (Fig. 56, *a*),* is constructed of such dimensions that it fits snugly into a Pyrex 100 × 12 mm. test-tube. The constricted end of the tube (2 mm. diameter) is partially packed with the filter medium with the aid of a 4 mm. glass rod. The filter media employed are purified cotton wool, " Gooch " asbestos, and glass wool or fibre (Corning brand, No. 790). The most satisfactory, and the least expensive, medium is cotton wool. Where cotton wool is unsuitable because of possible chemical reaction with the reagent, " Gooch " asbestos or glass wool is employed: the former must be very carefully packed, otherwise filtration will be extremely slow.



(a) (b)

Fig. 56.

To pack the pressure-filter tube with cotton wool, a small quantity of the latter is introduced and then pushed down into the constricted end with a 4 mm. glass rod (Fig. 56, *b*). The depth of the cotton wool will determine the retentiveness of the filter and the rate of filtration. After a little experience the amount required for most filtrations will be introduced at the first filling: as a general rule the packing will occupy 6–7 mm. of the narrow end (the weight is about 50 mg.). The cotton wool should be removed from the tube after each filtration by means of a nickel or monel metal wire of about 1 mm. diameter; a glass rod drawn out at one end to about 1 mm. can also be used.

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* This and the other semimicro apparatus described in this Chapter are obtainable from A. Gallenkamp and Co., Ltd., Sun Street, London, E.C. 2.

Certain finely-divided precipitates, such as those encountered in Groups IIIB and IV, are filtered with difficulty through cotton wool. This is readily overcome by packing the filter tube first with cotton wool to a depth of 6–7 mm. and then with "Gooch" asbestos to a depth of about 5 mm. This combined cotton wool-asbestos plug should always be employed when a turbid filtrate is obtained with cotton wool alone.

To carry out a filtration, the pressure-filter tube is packed with an appropriate filter medium (usually cotton wool) and inserted into a semimicro test-tube (100 × 12 mm.).* The solution to be filtered is poured into the filter tube and pressure is applied to the solution by means of a pressure bulb (Fig. 57). A rubber bulb of 3–4 ounces capacity† is fitted with a small rubber stopper through which passes a glass tube 10 cm. long and 4 mm. diameter and carrying a small rubber stopper at the other end. The rubber bulb is clamped at its lower end carrying the rubber stopper, and the pressure-filter tube and test-tube combination is placed in a small wooden stand. Pressure can then be applied by suitably compressing the rubber bulb. The filtrate will of course collect in the test-tube and the precipitate will remain on the cotton wool. If the filtrate is turbid, it must be passed again through the filter. Sometimes it may be necessary to repack the filtering medium ; should this prove ineffective, the cotton wool-asbestos medium, referred to above, should be used. A note of caution must be added. The pressure exerted on the bulb should not be too great as there is a danger that the solution may be blown out of the tube.

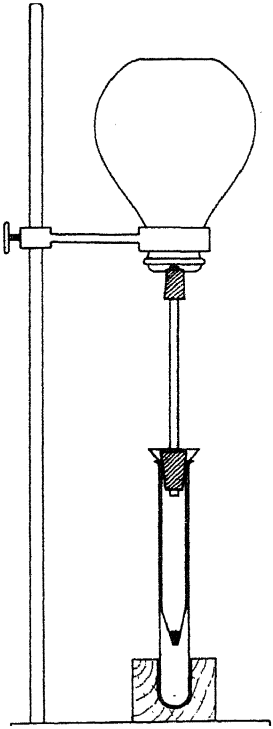

Fig. 57.

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* Pressure-filter tubes are also available which fit into the 75 × 10 mm. test-tubes (4 c.c.). These permit of interchange between the pressure-filter tube and centrifuge techniques, for most semimicro centrifuges will accommodate the smaller test-tubes.

† The author has found the bulb of a commercial rectum syringe quite satisfactory, but any other rubber bulb (*e.g.*, that of an ear syringe) will serve the same purpose.

The advantages of this method of filtration are :—

(1) The cost is very small so that each student may have a complete set of filtration apparatus.

(2) The filtration process is under observation all the time and can be readily controlled (by selection of the filter medium, thickness of the medium, and pressure applied to the rubber bulb).

(3) The solution can be kept hot during the filtration (see description of the Barber water bath rack below).

(4) The precipitate can be rapidly and efficiently washed, and is immediately available for further tests (dissolution, colour tests, etc.).

(5) Light and flocculent precipitates, which are not readily " centrifuged," are easily filtered.

Various methods may be used where more than 3 c.c. of suspension has to be filtered :

(i) Equal volumes of the suspension may be placed in both 3 c.c. centrifuge tubes.

(ii) A larger centrifuge tube (5 c.c.) may be employed since this will fit most semimicro centrifuges.

(iii) Equal volumes of the suspension may be placed in two 75 × 10 mm. test-tubes : the centrifuge is generally provided with an adaptor for these tubes.

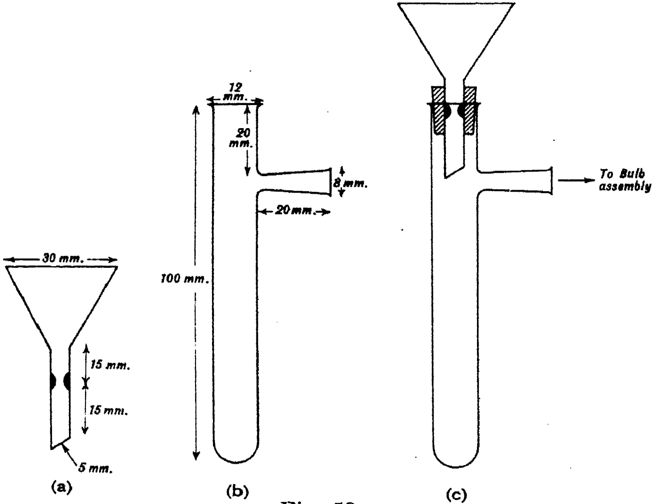

Fig. 58.

Another procedure utilises the Barber semimicro funnel and vacuum filter tube shown in Fig. 58. The constricted part of the semimicro funnel is packed with cotton wool, " Gooch " asbestos or Corning glass wool (No, 790) ; the depth and firmness of the packing of the filter medium determines the rate of filtration and the retentiveness of the filter. For filtration the bulb is depressed and inserted into the side arm of the vacuum filter tube which, if desired, may be made of somewhat larger capacity. If the semimicro analysis is properly carried out, the use of this assembly is rarely necessary.

Washing of the precipitate. It is essential to wash all precipitates in order to remove the small amount of solution present in the precipitate, otherwise it will be contaminated with the ions present in the filtrate. It is best to wash the precipitate at least twice and to combine the first washing with the filtrate. The wash liquid is a solvent which does not dissolve the precipitate, but dilutes the small quantity of mother liquor adhering to the precipitate ; it is usually water, but may be a dilute solution of an electrolyte since water sometimes tends to produce colloidal solutions (*i.e.*, to peptise the precipitate).

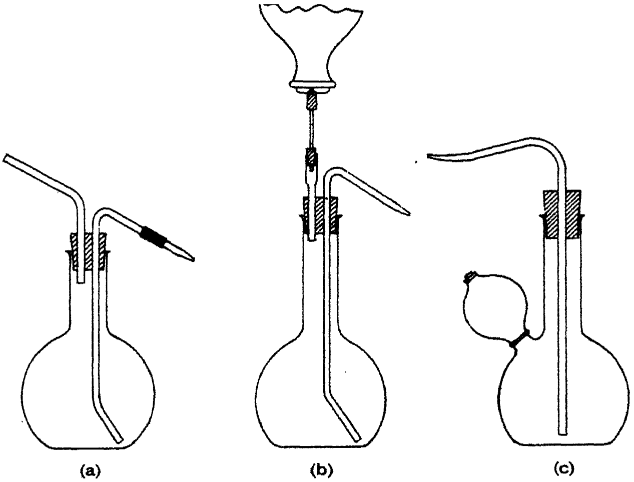
(a) (b) (c)

Fig. 59.

To wash a precipitate in a centrifuge tube, 5–10 drops of water or other reagent are added and the mixture thoroughly stirred : the centrifuge tube is then counterbalanced against another similar tube containing water to the same level and centrifuged. The liquid above the precipitate is removed by a capillary dropper as described above, and the washing repeated at least once.

The process is similar for a pressure-filter tube: 5–10 drops of the wash liquid are added and then slowly forced through the filter medium with the pressure bulb. The test-tube is then replaced by an empty one and the washing repeated. The second washing is usually discarded.

Wash bottles. For most work in semimicro analysis an ordinary 30 c.c. glass-stoppered bottle is a suitable container for distilled water, which may be handled with a reagent dropper. Alternatively, a bottle carrying its own dropper may be used. For hot water, a small (25 or 50 c.c.) conical flask may be employed. For those who prefer wash bottles various types are available (Fig. 59): *a* is 250–500 c.c. flat-bottomed flask *with the jet of 0·5–1 mm. diameter* and is mouth-operated; *b* is similar, but is hand-operated with a rubber bulb; *c* is a commercial form * of hand-operated wash bottle.

Transferring of precipitates. *From centrifuge tubes.* In some cases, this can be done with a semimicro spatula (two convenient types in nickel or monel metal are shown in Fig. 60). Where this is difficult, a wash liquid or the reagent to be employed is added, the mixture vigorously stirred and the resulting suspension transferred with a capillary dropper. If required, the liquid may then be removed by filtration by either of the methods previously described.

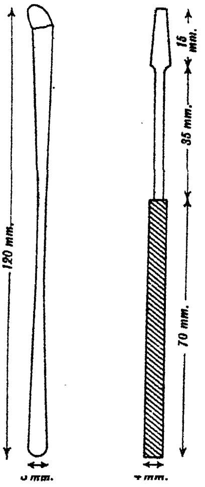

Fig. 60.

From pressure-filter tubes. The cotton wool (or other filter medium) is removed with the aid of a 1 mm. nichrome or monel metal wire or of an equivalent glass rod. The precipitate may either be scraped off with a spatula or the filter medium and precipitate may be kept together provided the subsequent reagent has no reaction on the filter medium.

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* Made by E. H. Sargent and Co., 155–165 E. Superior St., Chicago, Illinois, U.S.A.

† Obtainable from A. Gallenkamp and Co., Ltd., Sun Street, London, E.C. 2.

Heating of solutions. Solutions in semimicro test-tubes or centrifuge tubes cannot be heated over a free flame owing to the serious danger of "bumping" (and consequent loss of part or all of the liquid) in such narrow tubes. The most convenient apparatus for heating of solutions or of suspensions up to a temperature of 90–100° is Barber's water bath rack (Fig. 61).† The dimensions of a rack of suitable size are given in Fig. 62. This will accommodate 4 centrifuge tubes and 4 semimicro test-tubes. The apparatus is constructed of monel metal, or of brass which is subsequently tinned.* The rack is placed in a 250 c.c. beaker, the latter filled to within 1 cm. of the rim with distilled water, and heated on a wire gauze and tripod. It is recommended that a small rubber band be wound round each tube about 5 mm. from the top (see Fig. 61): this will facilitate handling of the hot tubes, and the rubber band may also be used for attaching small pieces of folded paper containing notes of contents, *etc.*

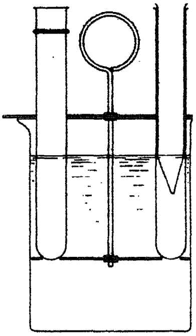

Fig. 61.

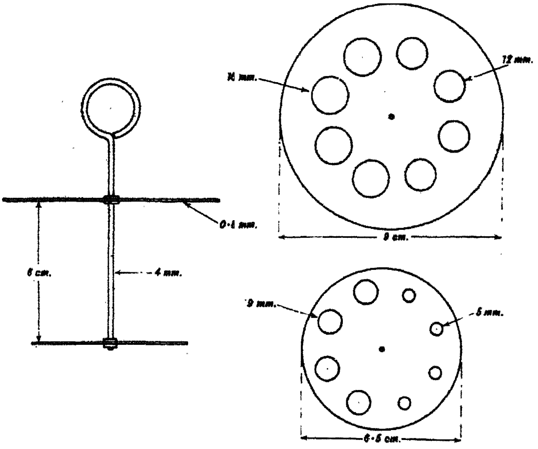

Fig. 62.

Evaporations. Where rapid concentration of a liquid is required or where volatile gases must be rapidly expelled, the semimicro boiling tube (*c* in Fig. 49) should be used. Two useful holders are shown in Fig. 63; *b* * is to be preferred as the boiling tube cannot fall out by mere pressure on the holder at the point where it is usually held. If evaporation to dryness is required, a small casserole (6 c.c.) or crucible (4–5 c.c.) may be used. This should be placed in an air bath consisting of a 30 c.c. nickel crucible and supported thereon by an asbestos ring (Fig. 64, *a*), and heated with a semimicro burner. Alternatively, a small Pyrex beaker (say, 100 c.c.) may be used and a triangle of nichrome wire employed to support it (Fig. 64, *b*).

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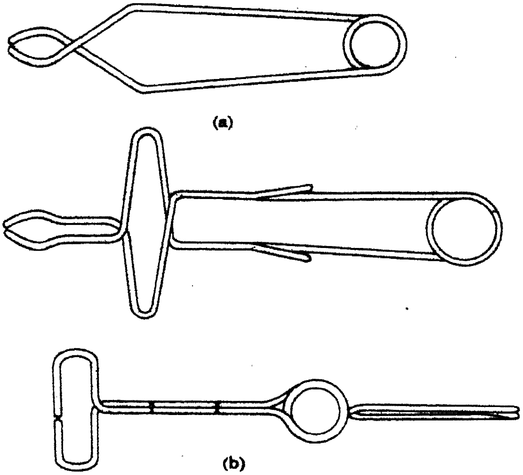
* The brass is most simply tinned by boiling with 20 per cent. NaOH solution containing a few lumps of metallic tin.


(a)

(b)

Fig. 63.

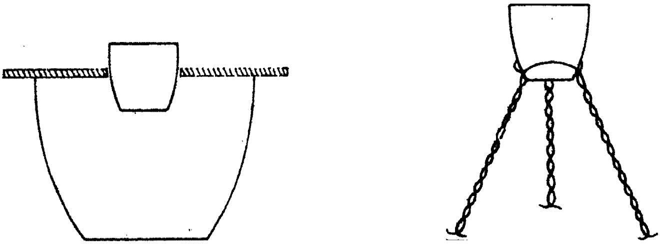

(a) (b)

Fig. 64.

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* Made by the Central Scientific Co., of 1700 Irving Park Blvd., Chicago, U.S.A., and termed the " Cenco Bi-Grip " test-tube clamp.

Dissolving of precipitates. *In centrifuge tubes.* The reagent is added and the suspension warmed, if necessary, on the water bath until the precipitate has dissolved. If only partial solution occurs, the suspension may be centrifuged.

In pressure-filter tubes. If the reagent has no action upon the filter medium (as is usually the case), it is added directly to the pressure-filter tube. If the precipitate dissolves readily, the solution is forced through the filter medium with the pressure bulb. However, if the precipitate dissolves slowly, the pressure-filter tube and surrounding test-tube may be placed in the water bath rack. The reagent is stirred with a semimicro stirring rod and allowed to flow through the filter medium under the force of gravity.

Another procedure is to place the pressure-filter tube containing the reagent in a semimicro boiling tube (Fig. 65) or in a 25 c.c. conical flask containing about 2 c.c. of water, and to heat with a free flame. The reagent is heated by the steam and causes the dissolution of part or all of the precipitate as the solution slowly passes through the filter medium. As soon as the precipitate (or the soluble portion) has dissolved the remainder may be forced through with a pressure bulb.

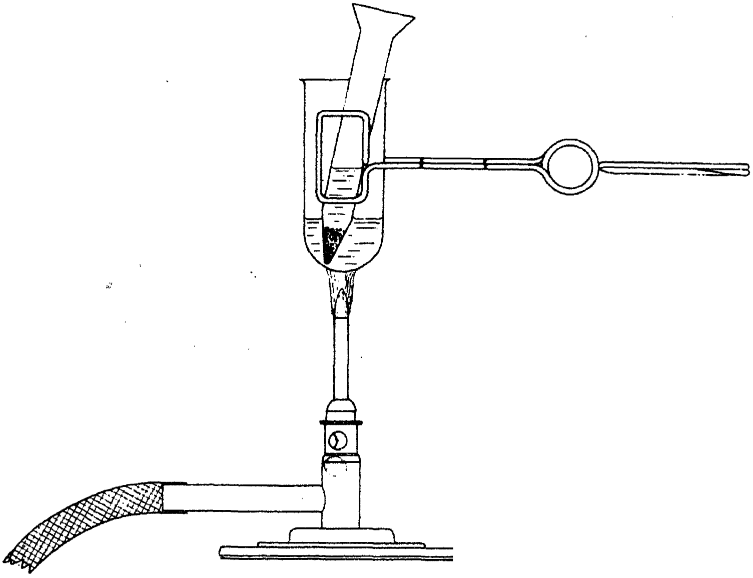


Fig. 65.

The filtrate is then in the boiling tube or conical flask, and may be concentrated or evaporated almost to dryness.

Yet another procedure which may be employed is to place the filter medium and precipitate in a semimicro boiling tube, add the reagent and heat over a micro flame until dissolved.

Cleaning of apparatus. It is essential to keep all apparatus scrupulously clean if trustworthy results are to be obtained. All apparatus must be thoroughly cleaned with cleaning mixture (a solution of sodium or potassium dichromate in concentrated sulphuric acid) or with a brush and cleaning powder. The apparatus is then rinsed several times with tap water, and repeatedly with distilled water. Special brushes (Fig. 66) are available for semimicro test-tubes and centrifuge tubes ; the commercial " pipe cleaners " are also satisfactory. The tubes may be allowed to drain in a special stand or else they may be inverted in a small beaker on the bottom of which there are several folds of filter paper or a filter paper pad to absorb the water. Larger apparatus may be allowed to drain on a clean linen towel or glass cloth. Droppers are best cleaned by first removing the rubber bulbs or teats and allowing distilled water to run through the tubes ; the teats are cleaned by repeatedly filling them with distilled water and emptying them. When clean, they are allowed to dry on a linen glass cloth. At the end of the laboratory period, the clean apparatus is placed in a box with cover, so that they may remain clean until required.

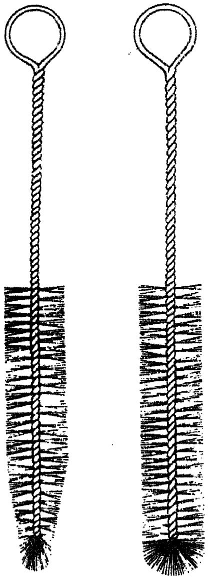


Fig. 66.

Spot plates. Drop reaction paper. These are employed chiefly for confirmatory tests (see Section **II, 5,** for a full discussion). Spot plates with a number of circular cavities are available either black or white. The former are employed for white or other light-coloured precipitates, and the latter for dark-coloured precipitates. Transparent spot plates and combination black and white spot plates (with line of demarcation between the black and white running exactly through the centres of the depressions) are also marketed. Spot plates are useful for testing the pH of a solution colorimetrically and also for mixing small quantities of reagents. Sometimes a pressure filter tube with filter medium may be used for spot tests.

Drop reaction or spot-test paper is a soft variety of pure, highly porous paper which is used for reactions that result in coloured precipitates. The precipitate cannot spread very far into the paper because of the filtering action of the pores of the paper ; consequently the spot-test technique is employed in highly sensitive identification tests, the white paper serving as an excellent background for dark or highly coloured precipitates and incidentally providing a permanent record of the test.

Precipitations with hydrogen sulphide. Various automatic generators of the Kipp type are marketed, and may be employed for groups of students. Because of the highly poisonous character of hydrogen sulphide, these are always kept in a fume cupboard (draught chamber or hood). If an individual generator is desired, a Pyrex test-tube (150 × 20 mm.) containing " Aitchtuess " or an equivalent mixture (essentially an intimate mixture of a solid hydrocarbon, sulphur and asbestos) is utilised ; this yields hydrogen sulphide when heated and the evolution of gas ceases when the source of heat is removed. The test-tube type of generator is shown in Fig. 67, *a*. The small hole is covered with the finger during the passage of the gas. The method is not strongly recommended because pressure precipitation is difficult and, if attempted, introduces an element of danger.

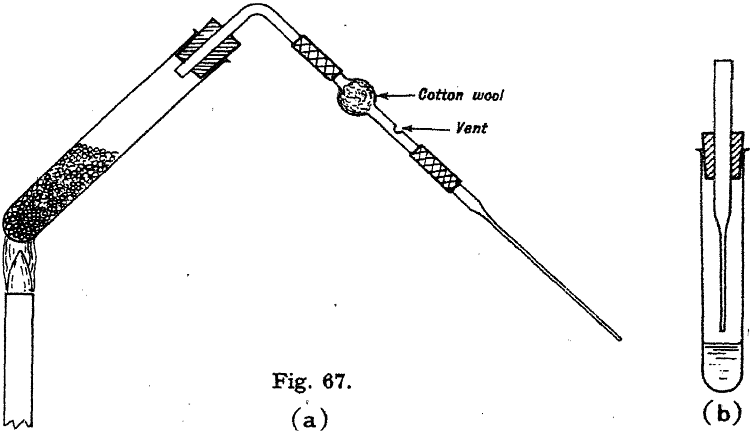


Fig. 67.

(a) (b)

A generator of the Kipp type is, on the whole, to be preferred. Precipitation is best carried out in a semimicro test-tube (100 × 12 mm.) or in a 10 c.c. conical flask ; for large volumes of solution a 25 c.c. Erlenmeyer flask may be necessary. The delivery tube is drawn out to a capillary (1–2 mm. in diameter) at the lower end and carries a rubber stopper at the upper end which fits the test-tube (Fig. 67, *b*) or conical flask. The delivery tube is connected to the source of hydrogen sulphide and a slow stream of the gas passed through the liquid for about 30 seconds in order to expel the air, the cork pushed into position, and the passage of hydrogen sulphide continued until very few bubbles pass through the liquid, the vessel being shaken gently from time to time. The tap in the gas generator is then turned off, and the delivery tube disconnected. If the liquid must be warmed, the cork is loosened, the vessel placed in the water bath for a few minutes, and the gas passed again.

Identification of evolved gases. Many anions (*e.g.*, carbonate, sulphide, sulphite, thiosulphate, and hypochlorite) are usually identified by the volatile decomposition products produced with the appropriate reagents. Suitable apparatus for this purpose are shown in Fig. 68. The simplest form *a* consists of a semimicro test-tube with the accompanying pressure-filter tube: a strip of test-paper (or of filter paper moistened with the necessary reagent) about 3–4 mm. wide is suspended in the pressure-filter tube. If it is desired to pass the maximum quantity of the evolved gas over the test-paper, the pressure bulb is depressed and inserted into the pressure-filter tube (as in *b*). In those

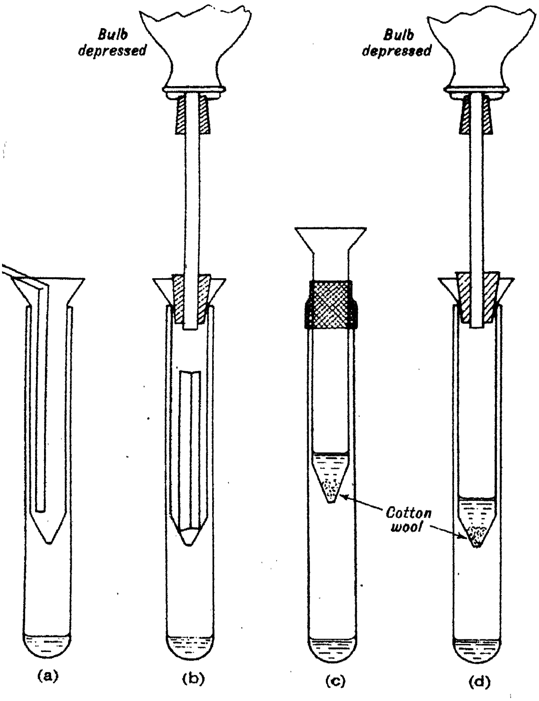


Fig. 68

cases where spray from the reaction mixture is likely to affect the test-paper, a *loose* cotton wool plug should be placed at the narrow end of the pressure-filter tube.

Apparatus *c* (Fig. 68) is employed where the test-reagent is a liquid. A short length of wide rubber tubing is fitted over the mouth of a semimicro test-tube with about 1 cm. protruding over the upper edge. The chemical reaction is started in the test-tube and a pressure-filter tube containing a tightly packed cotton wool plug inserted through the rubber collar, the filter plug again packed down with a 4 mm. glass rod, and 0·5–1 c.c. of the reagent introduced. In apparatus *d* the test-reagent is contained in the pressure filter tube carrying a tightly packed plug of cotton wool at the lower end, and the reaction mixture is in the test-tube. The evolved gas is forced through the reagent by inserting a depressed rubber bulb in the " funnel " of the pressure-filter tube.

All the above apparatus, *a–d*, may be warmed by placing in the hot water rack (Fig. 61). They will be found to meet all normal requirements for testing for gases evolved in reactions in qualitative analysis.

For those cases in which the amounts of evolved gases are likely to be small (so that it is best to sweep all the gases through the reagent by a stream of air) the apparatus of Fig. 69 will be found satisfactory. The approximate dimensions of the essential part of the apparatus are given in *a*, whilst the complete assembly is shown in *b*. The sample under test is

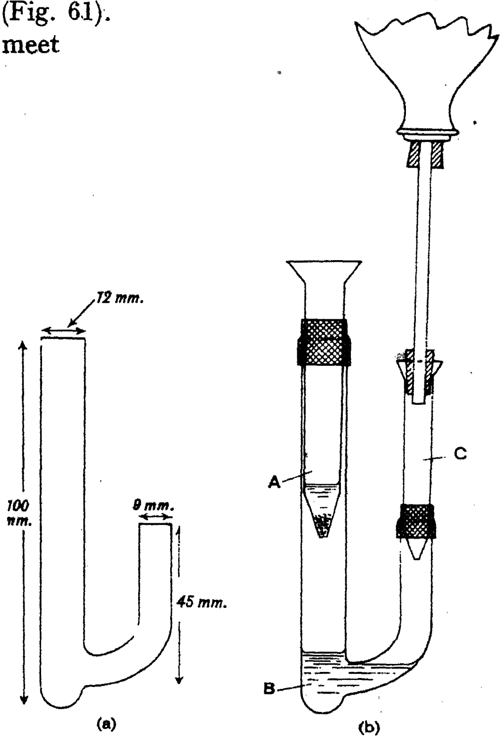


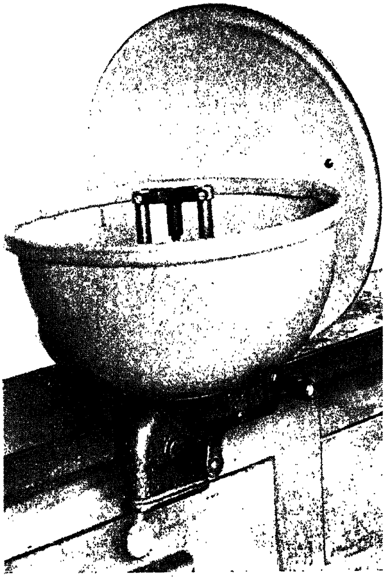
Fig. 69.

placed in *B*, the test-reagent is placed in the pressure-filter tube *A* over a tightly packed plug of cotton wool (or other medium), the acid or other liquid reagent is added through the pressure-filter tube *C*. The rubber bulb is inserted into *C* and by depressing it gently air is forced through the apparatus, thus sweeping out the gases from the reaction mixture through the test-reagent in *A*. The apparatus may be warmed by placing it in a hot water bath.

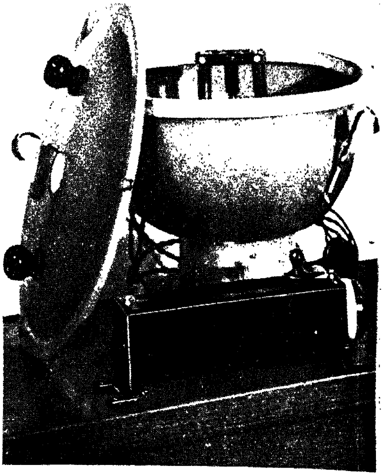
Semimicro apparatus. The plate (Fig. 70, *a* and *b*) shows all the general apparatus required for semimicro analysis, both by the centrifuge and pressure-filter tube methods. Other apparatus of specialised character will be described and illustrated in the text.

Calculation of the volume of precipitating agents. This type of calculation is instructive, for it will assist the student to fully appreciate the significance of the quantities of reagent employed in semimicro analysis. Let us assume that a sample contains 1 mg. of silver ions and 2 mg. of mercurous ions, and that the precipitating agent is 5*N* hydrochloric acid. To calculate the volume of the precipitating agent required, the number of equivalents of the ion or ions to be precipitated and the number of equivalents per c.c. of the precipitating agent must be ascertained. In the present sample there will be $1 \times 10^{-3}/107 \cdot 9 = 9 \cdot 3 \times 10^{-6}$ equivalents of silver ion and $2 \times 10^{-3}/200 \cdot 6 = 1 \times 10^{-5}$ equivalents of mercurous ion, *i.e.*, the total concentration of cation is $1 \cdot 93 \times 10^{-5}$ equivalents. Now 1 c.c. of 5*N* hydrochloric acid contains 5×10^{-3} equivalents of chloride ion, so that the volume of acid required will be $1 \cdot 93 \times 10^{-5}/5 \times 10^{-3} = 0 \cdot 0039$ c.c. The capillary dropper delivers a drop of about 0·03 c.c. (30–40 drops per c.c.), hence 1 drop of 5*N* hydrochloric acid contains sufficient chloride ions to precipitate the silver and mercurous ions and also to provide a large excess to reduce the solubility of the sparingly soluble chlorides (common ion effect).

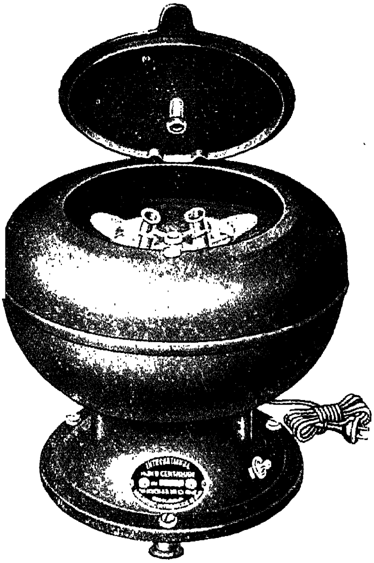
In practice, the weights of the ions in a solution of the sample are usually not known, so that exact calculations cannot be made. However, if the weight of sample employed is known, the maximum amount of precipitating agent required can be easily calculated. This is one of the reasons for taking a known weight (weighed to the nearest milligram) of the sample for analysis. Let us consider an actual example. We may assume that 50 mg. of the solid sample or, for solutions, such a volume as will yield 50 mg. of solid upon evaporation



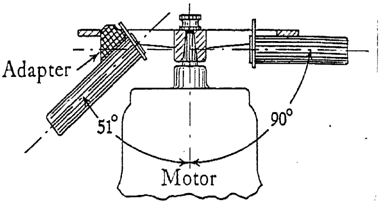
(i)



(ii)



(iii)



(i) Hand Centrifuge (*Moseley*)

(ii) Electric Centrifuge (*Moseley*)

(iii) Electric Centrifuge (*International*)

This is generally supplied for use on 110 volts A.C.; a resistance or resistance cord will be required for use on voltages of 200-240 A.C.

(iv) Rubber Adapter to convert (iii) for angle sedimentation (*diagrammatic*)

Fig. 70 (*b*)

to dryness, is taken for analysis and that the maximum quantity of all the metal ions present in the sample is 35 mg. It is evident that the smaller the equivalent of a given ion, the greater will be the number of equivalents contained in a given weight of it and hence the larger the volume of hydrochloric acid required for precipitation. In group I, lead has the lowest equivalent (103·5). The number of equivalents for 35 mg. of lead is $35/103{\cdot}5 \times 1000 = 3{\cdot}38 \times 10^{-4}$ equivalents or 0·338 milli-equivalents. Now 1 c.c. of $5N$ hydrochloric acid contains 5×10^{-3} equivalents or 5 milli-equivalents. Hence the exact volume of this acid required for complete precipitation is $0{\cdot}338/5 = 0{\cdot}0676$ c.c. = 2 drops, and the addition of 3–4 drops will suffice for complete precipitation (common ion effect) and also to prevent the precipitation of bismuth and antimony oxychlorides.

Some practical hints. (1) When transferring a liquid reagent with a reagent dropper, always hold the dropper just above the mouth of the vessel and allow the reagent to "drop" into the vessel. Do not allow the dropper tip to touch anything outside the reagent bottle; the possible introduction of impurities is thus avoided.

(2) Never dip your own dropper into a reagent bottle. Pour a *little* of the reagent (*e.g.*, concentrated acids and other corrosive liquids) into a small vessel (beaker, test-tube, crucible, etc.), and introduce your dropper into this. Never return the reagent to the bottle: it is better to waste a little of the reagent than to take the risk of contaminating the stock supply.

(3) Do not introduce your spatula into a reagent bottle to remove a little solid. Pour or shake a little of the solid on to a clean, dry watch glass, and use this. Do not return the solid reagent to the stock bottle. Try and estimate your requirements and pour out only the amount necessary.

(4) Keep your droppers scrupulously clean. Rinse the droppers several times with distilled water immediately after use. At the end of each laboratory period remove the rubber teat or cap and rinse it thoroughly.

IX, 2. SYSTEMATIC SEMIMICRO QUALITATIVE ANALYSIS OF INORGANIC SUBSTANCES

Introductory course. It is assumed that the student is already familiar with the dry reactions described in Section **II, 1,** and the tests detailed in Chapters III and IV as outlined in the Course of Instruction (Section **A, 4**). If the time available is very limited, the number of reactions studied may be reduced to those having an *immediate* bearing on the subsequent analysis and are given in Section **VIII, 6.** Reactions are generally carried out in semimicro test-tubes (100 × 12 mm. or 75 × 10 mm.). Where warming is necessary (say, up to 90°) a hot water bath (see Fig. 61) is used, but for higher temperatures (*e.g.*, boiling or concentration) a semimicro boiling tube (60 × 25 mm.) must be employed. Semimicro test-tubes (or centrifuge tubes) must on no account be heated in a free flame, for there is a serious danger of part or all of the contents " bumping " out of the narrow tube.

The preliminary experiments should be carried out with about 0·5 c.c. (*ca.* 12 drops) of test solutions, and reagents added with droppers. Filtration may be carried out either by the pressure-filter tube or centrifuge methods. Constant reference should of course be made to Chapters III and IV, where the reactions are given in detail, and the fact borne in mind that these are being carried out on $\frac{1}{10}$th to $\frac{1}{20}$th of the macro scale. For practice analysis of the various groups after the reactions of the individual ions have been carried out, the semimicro tables (headed *SM*) must be used.

The student must realise that the object of qualitative analysis is not simply to detect the constituents of a given mixture ; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose about 0·2 gram of material is usually employed for the analysis : the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

Every analysis is divided into three parts :

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions). A special preliminary test for nitrate and/or nitrite is also made here.

(2) *The examination for acid radicals (or anions) in solution.*

(3) *The examination for metal ions (or cations) in solution.*

IX, 3. PRELIMINARY TESTS

Test (i). Heating in a closed tube.—Place about 20 mg. of the substance in a dry ignition tube (70 × 4–5 mm.) so that none of it remains adhering to the sides and heat cautiously with a semimicro burner; the tube should be held in an almost horizontal position. Raise the temperature gradually and carefully note any changes which take place.

[*Table on p.* 508]

Test (ii). Charcoal block reductions.—

(*a*) Heat a little of the substance in a small cavity in a charcoal block in a blowpipe flame.

Observation	*Inference*
1. The substance decrepitates.	Crystalline salts, as NaCl, KCl.
2. The substance deflagrates.	Oxidising agents, *e.g.*, nitrates, nitrites, and chlorates.
3. The substance is infusible or incandescent, or forms an incrustation upon the charcoal.	Apply test (*b*) below.

(*b*) Mix the substance with twice its bulk of anhydrous sodium carbonate, place it in a cavity in a charcoal block, and heat in the reducing flame of the blowpipe.

Observation	*Inference*
1. Incrustation without metal:	
White, yellow when hot.	ZnO.
White, garlic odour.	As_2O_3.
Brown.	CdO.
2. Incrustation with metal:	
White incrustation; brittle metal.	Sb.
Yellow incrustation; brittle metal.	Bi.
Yellow incrustation; grey and soft metal, marks paper.	Pb.
3. Metal without incrustation:	
Grey metallic particles, attracted by magnet.	Fe, Ni, Co.
Malleable beads.	Ag and Sn (white); Cu (red flakes).

Observation	*Inference*
(a) A gas or vapour is evolved.	
1. Water is evolved; test with litmus paper.	Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts and hydroxides.
The water is alkaline.	Ammonium salts.
The water is acid.	Readily decomposable salts of strong acids.
2. Oxygen is evolved (rekindles a glowing splint).	Nitrates, chlorates, and certain oxides.
3. Nitrous oxide (rekindles glowing splint) and steam are evolved.	Ammonium nitrate or nitrate mixed with an ammonium salt.
4. Dark brown or reddish fumes (oxides of nitrogen); acidic in reaction.	Nitrates or nitrites of heavy metals.
5. Carbon dioxide is evolved (lime water is rendered turbid).	Carbonates or bicarbonates.
6. Ammonia is evolved (turns red litmus paper blue).	Ammonium salts.
7. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green).	Normal and acid sulphites; thiosulphates; certain sulphates.
8. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black).	Hydrated sulphides or sulphides in the presence of water.
9. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); *very poisonous*.	Unstable chlorides, *e.g.*, of copper; chlorides in the presence of oxidising agents.
10. Bromine is evolved (reddish-brown vapour; choking odour).	Sources similar to chlorine.
11. Iodine is evolved (violet vapours condensing to black crystals).	Free iodine and certain iodides.
(b) A sublimate is formed.	
1. White sublimate*.	Ammonium and mercuric salts; As_2O_3; Sb_2O_3.
2. Grey sublimate, easily rubbed to globules.	Hg.
3. Steel-grey sublimate; garlic odour.	As.
4. Yellow sublimate.	S (melts on heating), As_2S_3, HgI_2 (red when rubbed with a glass rod).

* If a white sublimate forms, heat with four times the bulk of anhydrous Na_2CO_3 and a little KCN in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates *Hg* (*Note*: Hg vapour is *very poisonous*); a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates *As*; ammonia evolved (test with mercurous nitrate paper) indicates ***ammonium salts***.

Test (iii). Flame colourations.—Place a few milligrams of the substance in a depression of a spot-plate, moisten with a few drops of concentrated hydrochloric acid, and introduce a little of the substance on a *clean* platinum wire into the base of a non-luminous flame of a semimicro burner. Alternatively, dip the platinum wire into concentrated hydrochloric acid contained in a depression of a spot plate and then into the substance ; sufficient will adhere to the platinum wire for the test to be carried out.

Observation	*Inference*
Persistent golden-yellow flame.	Na.
Violet (lilac) flame (crimson through cobalt-blue glass).	K.
Brick-red (yellowish-red) flame.	Ca.
Crimson flame.	Sr.
Yellowish-green flame	Ba.
Livid-blue flame (wire slowly corroded)	Pb, As, Sb, Bi, Cu.

The sodium flame masks that of other elements, *e.g.*, that of potassium. Mixtures can be readily detected with a direct-vision spectroscope. A less delicate method is to view the flame through two thicknesses of cobalt-blue glass, whereby the yellow colour due to sodium is masked or absorbed ; potassium then appears crimson.

Test (iv). Borax bead reactions.—Make a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead

Oxidising Flame	*Reducing Flame*	*Metal*
1. Green when hot ; blue when cold.	Colourless or opaque when cold.	Cu.
2. Yellow, hot and cold.	Green, hot and cold.	Fe.
3. Green, hot and cold.	Green, hot and cold.	Cr.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Mn.
5. Blue, hot and cold.	Blue, hot and cold.	Co.
6. Reddish-brown when cold.	Grey when cold.	Ni.

in the inner or reducing flame and observe the colour in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, nickel and cobalt; the most characteristic result is for cobalt.

Test (v). Test for ammonium radical.—Mix 10–20 mg. of the substance with about 0·5 c.c. of sodium hydroxide solution in a semimicro test-tube, introduce a pressure-filter tube carrying a strip of red litmus paper,* and place the assembly (see *a* in Fig. 68) in the hot water rack (Fig. 61). Alternatively, apparatus *b* in Fig. 68 may be employed. The evolution of ammonia, detected by its action upon the reagent paper, indicates the presence of an *ammonium salt.*

Test (vi). Test for nitrate (or nitrite).—If ammonium is found, transfer the solution from test (v) to a semimicro boiling tube, add 1 c.c. each of sodium hydroxide solution and of water, and evaporate down to a volume of 0·5 c.c.—this treatment completely decomposes the ammonium salt. Transfer the residue to a semimicro test-tube, add 1 c.c. of sodium hydroxide solution and 20 mg. of Devarda's alloy (or of aluminium as powder or thin foil), introduce a pressure-filter tube containing a plug of cotton wool at the lower end and a strip of red litmus paper or of mercurous nitrate paper (Fig. 68, *a*), and place the assembly in the hot water rack. (If the proportion of nitrate or nitrite is small, the apparatus shown in Fig. 68, *b*, is recommended.) When frothing occurs, remove the apparatus from the water bath until the vigorous action has subsided.

If ammonium is absent, add about 20 mg. of Devarda's alloy (or of aluminium as powder or thin foil) and 0·5 c.c. of sodium hydroxide solution to the reaction mixture from test (v), introduce the pressure-filter tube containing the reagent paper, and proceed as above. If ammonia is evolved, as detected by its action upon red litmus paper or upon filter paper moistened with mercurous nitrate solution then the presence of *nitrate or nitrite* is indicated. The presence of nitrite will generally also be detected in the reaction with dilute sulphuric acid (see test (vii)); if nitrite is absent, then the presence of nitrate alone is established.

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* Filter paper soaked in mercurous nitrate solution may also be used; this is blackened by ammonia. Since mercurous nitrate solution reagent usually contains an excess of free nitric acid, it is recommended that sodium carbonate solution be added to about 1 c.c. of mercurous nitrate solution until a *slight* permanent precipitate is produced, and the filtered solution be employed for the preparation of the mercurous nitrate paper.

It must be emphasised that the mercurous nitrate paper test for ammonia is not applicable in the presence of arsenites. Arsenites are reduced under the above conditions to arsine, which also blackens this test paper.

Test (vii). Action of dilute sulphuric acid.—Treat 10–20 mg. of the substance in a semimicro test-tube with about 0·5 c.c. of dilute sulphuric acid and note whether any reaction takes place in the cold (indicated by *C*). Warm gently and observe the effect produced.

Observation	*Inference*
1. Colourless gas is evolved with effervescence; gas is odourless and produces a turbidity when passed into lime water (see Fig. 43). (*C*)	CO_2 from *carbonate.*
2. Nitrous fumes evolved; recognised by reddish-brown colour and odour. (*C*)	NO_2 from *nitrite.*
3. Yellowish-green gas evolved; suffocating odour, reddens then bleaches litmus paper, also turns starch-KI paper blue; *very poisonous.* (*C*)	Cl_2 from *hypochlorite.*
4. Colourless gas evolved with suffocating odour; turns filter paper moistened with $K_2Cr_2O_7$ solution green.	SO_2 from *sulphite.*
5. Colourless gas evolved; gives above tests for SO_2; sulphur is deposited in the solution.	SO_2 and S from *thiosulphate.*
6. Colourless gas evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution.	H_2S from *sulphide**.
7. Odour of vinegar.	$H.C_2H_3O_2$ from *acetate.*
8. Colourless gas is evolved; rekindles glowing splint.	O_2 from *peroxides* of alkali and alkaline earth metals.

Test (viii). Action of concentrated sulphuric acid.—Treat 10–20 mg. of the substance in a semimicro test-tube with 0·5 c.c. of concentrated sulphuric acid. If no reaction occurs in the cold, place the tube in the hot water rack. (If chlorate is suspected from the preliminary charcoal reduction test to be present, use not more than 5 mg. for this test, as an explosion may result on warming.)

If the substance reacted with dilute sulphuric acid, the addition of the concentrated acid may result in a vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of acid. In such a case it is best to add dilute sulphuric acid from a capillary dropper to another portion of the substance until action ceases, and then to add 1 c.c. of concentrated sulphuric acid.

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* Many sulphides, especially native ones, are not affected by dilute H_2SO_4; some H_2S is evolved by warming with concentrated HCl alone or with a little tin.

Observation	*Inference*
1. Colourless gas evolved with pungent odour and which fumes in the air; white fumes of NH_4Cl in contact with glass rod wet with NH_4OH solution; Cl_2 evolved on addition of MnO_2 (reddens then bleaches litmus paper).	HCl from *chloride*.
2. Gas evolved with pungent odour, reddish colour, and fumes in moist air; on addition of MnO_2 increased amount of red fumes with odour of Br_2 (fumes colour filter paper moistened with fluorescein solution red).	HBr and Br_2 from *bromide*.
3. Violet vapours evolved, accompanied by pungent acid fumes, and often SO_2 and even H_2S.	HI and I_2 from *iodide*.
4. Yellow gas evolved in the cold with characteristic odour; explosion or crackling noise on warming *gently* (**DANGER !**).	ClO_2 from *chlorate*.
5. "Oily" appearance of tube in cold; on warming, pungent gas evolved, which corrodes the glass; if moistened glass rod introduced into the vapour, a gelatinous precipitate of hydrated silica is deposited upon it.	HF from *fluoride*.
6. Colourless gas evolved; burns with a blue flame *; no charring (*very poisonous*).	CO from *formate*.

IX, 4. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary tests (vii) and (viii) with dilute sulphuric acid and with concentrated sulphuric acid will have provided useful information as to many acid radicals present. For more detailed information, it is necessary to have a solution containing all (or most) anions free from heavy metals. This is best prepared by boiling the substance with concentrated sodium carbonate solution; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates † of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution. Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur :

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* The burning splint should be introduced *into* the tube; the application of a flame to the mouth of the tube frequently fails to ignite the gas owing to its dilution with air in the tube.

† Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.

$$MA_2 + Na_2CO_3 \rightleftharpoons MCO_3 + 2NaA.$$

The carbonate MCO_3 is insoluble and the sodium salt NaA will pass into solution whether MA_2 is soluble in water or not.

Preparation of solution for testing for anions.—Boil 200 mg. of the finely-divided substance or mixture with 2·5 c.c. of a saturated solution of pure sodium carbonate * (prepared from 0·4 g. of anhydrous sodium carbonate and 2·5 c.c. of distilled water) for 5–10 minutes in a 10 c.c. conical flask with a funnel in the mouth to reduce the loss by evaporation. Filter † (using a pressure-filter tube with a cotton wool-asbestos plug or a centrifuge), wash the residue with hot distilled water, and collect the washings together with the main filtrate ; the total volume should be 3–4 c.c. Reject the residue. The sodium carbonate extract will be termed the "*prepared*" solution. Use the solution to carry out the following tests.

1. Sulphate test.—To 10 drops of the "prepared" solution add dilute hydrochloric acid until acid (test with litmus paper) and then add 5 drops in excess. Place in the hot water rack for 5 minutes to expel carbon dioxide completely, and then add 3–4 drops of barium chloride solution. A white precipitate ($BaSO_4$) shows the presence of *sulphate.*

2. Test for reducing agents.—Acidify 10 drops of the "prepared" solution with dilute sulphuric acid and add 5 drops of dilute sulphuric acid in excess. Add 3–4 drops of $0 \cdot 02N$ potassium permanganate solution (prepared by dilution of 1 drop of $0 \cdot 1N$ $KMnO_4$ with 4 drops of water and mixing well). Bleaching of the permanganate solution indicates the presence of one or more of the following reducing anions : *sulphite, thiosulphate, sulphide, nitrite, bromide, iodide and arsenite.* If the permanganate is not decolourised, place the tube in the hot water rack for several minutes and observe the result. If the reagent is bleached only on heating, the presence of *oxalate* is indicated. A negative test shows the absence of the above anions.

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* It is essential to use pure sodium carbonate ; the A.R. solid is satisfactory. Some "pure" samples may contain traces of sulphate or chloride : the absence of these impurities should be confirmed by a blank experiment.

† If no precipitate is obtained, the substance is virtually free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required.

3. Test for oxidising agents.—Acidify 10 drops of the "prepared" solution cautiously with concentrated hydrochloric acid and add 5 drops in excess, followed by 5–10 drops of the manganous chloride reagent. Place in the hot water rack for 1 minute. A brown (or black) colouration indicates the presence of *nitrate, nitrite, chlorate or chromate.* A negative test indicates the absence of the above oxidising anions except for small amounts of nitrates or nitrites. If reducing anions have been found, the test is inconclusive.

Note. The **reagent** consists of a saturated solution of manganous chloride, $MnCl_2,4H_2O$, in concentrated hydrochloric acid. Its action depends upon its conversion by even mild oxidising agents to a dark-brown coloured manganic salt, probably containing the complex $[MnCl_6]^{--}$ or $[MnCl_4]^{--}$ ions.

4. Test with silver nitrate solution.—Acidify 0·5–1 c.c. of the "prepared" solution cautiously with dilute nitric acid (use litmus paper). Determine the total volume of the acidified solution with the aid of a small measuring cylinder or of a calibrated 2 c.c. pipette, add one-tenth of the volume of concentrated nitric acid, transfer to a semimicro boiling tube, and boil gently for 30–60 seconds to expel carbon dioxide and other volatile gases ; * filter, if necessary, and allow to cool. Use the solution, the volume of which should be about 2 c.c., to carry out the tests given in the following table.

Notes. (1) It is essential that the solution be just neutral to litmus or, at most, barely alkaline ; the latter will be indicated by a very slight brown opalescence (due to Ag_2O) obtained after shaking. If much brown silver oxide separates, it will re-dissolve only with difficulty.

The introduction of 1 drop of nitrazine yellow indicator into the solution is to be preferred. (This indicator covers the *p*H range 5·5–7·2 and the colour change is from yellow to blue.) The addition of NaOH solution is continued until the solution just assumes a pale blue colour.

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* If H_2S or SO_2 is evolved, partial oxidation to sulphuric acid will occur. Arsenite, if present, will also be largely oxidised to arsenate, hence no provision for the identification of arsenite is made in the table. Iodides will be partially oxidised by the nitric acid to iodine, which will be readily identified by the brown colour of the solution ; the presence of iodide will also have been indicated in the preliminary test with concentrated sulphuric acid. Bromides are only slightly oxidised to bromine by the nitric acid of the concentration employed (*ca.* 1·5*N*).

<table>
<tr><td colspan="3">Add 3 drops of concentrated HNO_3, followed by a few drops of $AgNO_3$ solution. If a ppt. forms, place in the hot water rack and add $AgNO_3$ solution slowly and with stirring until precipitation is complete. (If no ppt. forms, do not add more $AgNO_3$ solution.) Filter (pressure-filter tube or centrifuge) and wash with very dilute HNO_3 (1 : 20).</td></tr>
<tr><td rowspan="2">Residue.
AgCl white.
AgBr pale yellow.
AgI yellow.</td><td colspan="2">Filtrate. Add 2–3 drops of $AgNO_3$ solution and divide the solution (<i>A</i>) into two unequal parts.
To the smaller portion add 2–3 drops of 20% $NaNO_2$ solution (chloride-free). If a white ppt. (AgCl) forms, the presence of chlorate is indicated. If chlorate is present, treat the remainder of the solution <i>A</i> with 6 drops of $AgNO_3$ solution, 3 drops of dilute HNO_3, followed by $NaNO_2$ solution until precipitation is complete. Filter off the AgCl and keep the filtrate (<i>B</i>).
To filtrate <i>B</i> (if chlorate is present), or to the larger portion of <i>A</i> (if chlorate is absent), add NaOH solution drop-wise and with vigorous stirring until the solution is just neutral to litmus or, better, barely alkaline to nitrazine yellow indicator (1), then add 2–3 drops of dilute acetic acid and 5 drops of $AgNO_3$ solution, and heat to about 80° (2). If a permanent ppt. forms, add more $AgNO_3$ solution until precipitation is complete. Place in the hot water rack, filter (pressure-filter tube or centrifuge), and wash with hot water.</td></tr>
<tr><td>Residue.
Ag_3PO_4 yellow.
Ag_3AsO_4 reddish-brown (3)
$Ag_2C_2O_4$ white.
Ag_2CrO_4 scarlet (4).</td><td>Filtrate.
Reject.</td></tr>
</table>

(2) Silver acetate is soluble in hot water and is thus held in solution.

(3) Arsenite, if present, will be oxidised by the nitric acid treatment largely to arsenate so that little or no yellow silver arsenite Ag_3AsO_3 will separate here. Arsenite, however, will be readily identified in the analysis for cations by the immediate precipitation of arsenious sulphide As_2S_3 in dilute acid solution. Hence, if no arsenite is found in Group IIB, the presence of arsenate is indicated. It is assumed that the analysis of a mixture of arsenite and arsenate is outside the scope of an elementary course.

(4) If chlorate is present, the sodium nitrite treatment will reduce the chromate (indicated by a yellow or orange solution in *A* or *B*) to green chromic hydroxide, which will precipitate here. In the absence of a chlorate (*i.e.*, when the sodium nitrite treatment has been omitted), scarlet Ag_2CrO_4 is obtained if a chromate is present.

The separations described in the above table are based upon the following facts :—

(i) $AgNO_3$ solution precipitates only AgCl, AgBr and AgI from a dilute nitric acid solution, the other silver salts being soluble.

(ii) $NaNO_2$ solution reduces chlorate to chloride, which is precipitated as AgCl in the presence of $AgNO_3$ solution :

$$NaClO_3 + 3NaNO_2 = NaCl + 3NaNO_3.$$

(iii) In solutions faintly acid with acetic acid, phosphate, arsenate, arsenite, chromate and oxalate are precipitated by $AgNO_3$ solution.

5. Test with calcium chloride solution.*—For this and also for test *6* a " *neutral* " solution is required. This is prepared as follows. Take 1 c.c. of the " prepared " solution in a semimicro boiling tube and render it faintly acid with dilute nitric acid (use litmus paper). Heat to boiling for about 30 seconds to expel carbon dioxide, allow to cool, then add dilute ammonium hydroxide solution until just alkaline † and boil until the evolution of ammonia ceases. Transfer the " neutral " solution to a semimicro test-tube and divide into two equal parts ; reserve half for test *6*.

Add $CaCl_2$ solution (equal in volume to that of the solution) and allow to stand in the hot water rack for 5 minutes. Filter (pressure-filter tube with cotton wool-asbestos plug or by centrifuge).

Residue. May be calcium fluoride, oxalate, phosphate and arsenate. Extract with 1 c.c. of dilute acetic acid and filter.	**Filtrate.** Reject.

Residue. May be calcium oxalate and calcium fluoride. Extract with 1 c.c. of hot dilute H_2SO_4 and filter, if necessary. Treat the hot filtrate or solution with 2 drops of $KMnO_4$ solution. If the permanganate is decolourised, **oxalate is present.** If the ppt. is not completely soluble in dilute H_2SO_4, test original substance for fluoride by water film test (Section **IX, 5**).	**Filtrate.** Add NaOH solution drop-wise until neutral (use litmus or nitrazine yellow). White ppt. **Arsenate and/or phosphate present.**

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* Tests *5* and *6* may be omitted by those requiring only a beginner's course in qualitative analysis.

† If a ppt. forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric bases (lead, tin, aluminium and zinc) is indicated. The ppt. should be filtered off and rejected.

6. Test with ferric chloride solution.—Treat the other portion of the " neutral " solution from test *5* with a few drops of aqueous $FeCl_3$ solution.*

Reddish-purple colouration indicates *thiosulphate*.

Reddish-brown colouration, yielding a brown precipitate on dilution and boiling in a semimicro boiling tube, indicates *acetate*.

Yellowish-white precipitate indicates *phosphate*.

Blood-red colouration, discharged by $HgCl_2$ solution, indicates *thiocyanate*.†

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* The bench reagent usually contains excess of free acid added during its preparation in order to produce a clear solution ; this may prevent the precipitation of the basic acetate on boiling. It is recommended that Na_2CO_3 solution be added to 1 c.c. of the side-shelf $FeCl_3$ solution until a slight precipitate forms ; this is filtered off and the filtrate employed for the test with the " neutral " solution.

† Thiocyanate is not normally encountered in an elementary course and is given here for the sake of completeness and because of the characteristic nature of the test.

IX, 5. CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

The tests in the preceding section will indicate the acid radicals or anions present. In general, these should be confirmed by at least one distinctive confirmatory test. The following are recommended. Full experimental details will be found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (**IV, 2,** 7) is to be interpreted as Section **IV, 2,** reaction 7. It will of course be realised that the tests in Chapter IV refer to reactions on the macro scale; the student should have no difficulty in reducing these to the semimicro scale when once the technique described in Section **IX, 1** has been acquired. Particular attention is directed to the apparatus shown in Fig. 68, which is employed in testing for evolved gases with reagent papers and liquid reagents. It is assumed that interfering anions are absent or have been removed as described in Section **IX, 6** under *Special Tests for Mixtures of Acid Radicals.*

Chloride. Mix 20 mg.* of the substance with an equal weight of MnO_2 and 0·5 c.c. of concentrated H_2SO_4, and place in the hot water rack; Cl_2 evolved (reddens then bleaches litmus paper and also turns KI-starch paper blue) (**IV, 14,** *2*).

Bromide. MnO_2 and concentrated H_2SO_4 test (as under *Chloride*); Br_2 evolved (**IV, 15,** *2*) OR dissolve 20 mg. of the substance in 0·5 c.c. of water, add 5 drops of dilute HCl, 5 drops of CCl_4 and 2–3 drops of NaOCl solution and shake; reddish-brown colouration of CCl_4 layer (**IV, 15,** *5*).

Iodide. NaOCl solution, dilute HCl and CCl_4 test (as under *Bromide*); violet colouration of CCl_4 layer (**IV, 16,** *4*).

Fluoride. Fit a 100 × 12 mm. test-tube with a cork carrying a tube about 10 cm. long and of about 3 mm. bore: cut a V-shaped groove in the cork. Adjust the tube in the cork so that the lower end is about 2·5 cm. from the bottom of the test-tube (compare Fig. 46). Place 20–30 mg. of the substance and 0·5 c.c. of concentrated H_2SO_4 in the test-tube, dip the glass tube into water so that a film of water almost seals the lower end to a depth of about 5 mm., insert into the test-tube, and place in the hot water rack. The formation of a white film in the water confirms *fluoride* (**IV, 17,** *1*).

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* The weights and volumes given in the suggested confirmatory tests are very approximate and serve to indicate a reasonable scale for the various operations. They are given solely for the guidance of the student; satisfactory results can, however, be obtained on an appreciably smaller scale.

Nitrite. Treat 10–20 mg. of the substance with 0·5 c.c. of dilute acetic acid, 10 mg. of thiourea and 3 drops of $FeCl_3$ solution. Red colouration (**IV, 7,** *9*).

Nitrate. Brown ring test with $FeSO_4$ solution and concentrated H_2SO_4 (**IV, 18,** *3*) if bromide, iodide, chlorate and nitrite absent. (i) Dissolve 10–20 mg. of the substance in 0·5 c.c. of water. Cautiously add 1 c.c. of concentrated H_2SO_4, mix, and cool under running water. Incline the tube and with great care allow about 0·5 c.c. of $FeSO_4$ solution to run slowly down the side of the tube so that it forms a layer above the heavy sulphuric acid (Fig. 71). Observe the brown ring at the junction of the two liquids after 1–2 minutes. (ii) Dissolve 10–20 mg. of the substance in 0·5 c.c. of water and add about 1 c.c. of $FeSO_4$ solution. Incline the tube and allow 0·5–1 c.c. of concentrated H_2SO_4 to run slowly down the side of the tube to form a layer under the solution (Fig. 71), and after 1–2 minutes observe the brown ring at the interface.

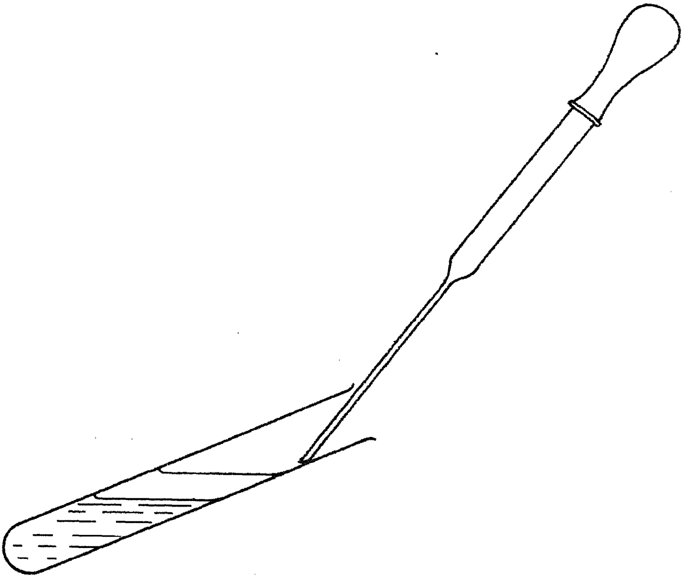

Fig. 71.

Sulphide. Treat 10–20 mg. of the substance with 0·5 c.c. of dilute H_2SO_4. Place the tube in the hot water rack and test with lead acetate paper (**IV, 6,** *1*).

Sulphite. Treat 10–20 mg. of the substance with 0·5 c.c. of dilute H_2SO_4, place the tube in the hot water rack, and test for SO_2 with $K_2Cr_2O_7$ paper * (Fig. 68, *a*) or with 0·5 c.c. of dilute $K_2Cr_2O_7$ solution (Fig. 68, *c*) (**IV, 4,** *1*).

Thiosulphate. Dilute H_2SO_4 on solid and liberation of SO_2 ($K_2Cr_2O_7$ test—details under *Sulphite*) *and* sulphur (**IV, 5,** *1*).

Sulphate. The $BaCl_2$ solution and dilute HCl test is fairly conclusive.

Further confirmation is obtained as follows. *Pressure-bulb technique.* Filter off the warm suspension of the precipitate through a cotton wool plug and wash with 1 c.c. of water. Transfer the filter plug to an ignition tube, add 2 drops of Na_2CO_3 solution, and cautiously heat to redness. Maintain the lower part of the tube at a red heat for 3–4 minutes, and allow to cool. Break the tube, transfer the charred residue as completely as possible to a semimicro test-tube, add 0·5 c.c. of dilute HCl, introduce a pressure-filter tube carrying a strip of filter paper moistened with lead acetate solution, and place the assembly in the hot water rack. A brown stain on the paper confirms **sulphate.**
Centrifuge technique. Centrifuge the precipitate and remove the supernatant liquid. Add 1 c.c. of water, stir, centrifuge, and discard the centrifugate. Add 3–4 drops of water, stir thoroughly to produce a fairly uniform suspension, transfer the suspension to a small plug of cotton wool in an ignition tube, and proceed as above.

Carbonate. Treat 10–20 mg. of the substance with 0·5 c.c. of dilute H_2SO_4, place the tube in the hot water rack, and test with 0·5 c.c. of lime water (Fig. 68, *c*) (**IV, 2,** *1*).

Hypochlorite. Treat 10–20 mg. of the substance with 0·5 c.c. of dilute HCl, place the tube in the hot water rack, and test for Cl_2 with KI-starch paper and with litmus paper (**IV, 13,** *4*).

Chlorate. The $AgNO_3$–$NaNO_2$ test is conclusive (see table in Section **IX, 4**).

Chromate. Mix 10–20 mg. of the substance with 0·5 c.c. of dilute H_2SO_4, add 0·5–1 c.c. of amyl alcohol and 0·5 c.c. of 10-volume H_2O_2 ; blue colour of alcohol layer (**IV, 33,** *4*).

Arsenite. Immediate ppt. of As_2S_3 in dilute HCl solution (**III, 11,** *1*) and absence of ppt. with magnesia mixture (**III, 11,** *3*).

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* For the preparation of $K_2Cr_2O_7$ paper, the dichromate solution should be almost saturated.

Arsenate. Action of H_2S on acid solution (**III, 12,** *1*), $AgNO_3$ solution test in faintly acetic acid solution (**III, 12,** *2*), and magnesia mixture test (**III, 12,** *3*).

Phosphate. Mix 10–20 mg. of the substance with 0·5 c.c. of dilute HNO_3, add 1 c.c. of ammonium molybdate reagent, and place the tube in the hot-water rack for a minute or two. Yellow ppt. (**IV, 28,** *4*).

Acetate. Mix 20 mg. of the substance with 1 c.c. of ethyl or *n*-butyl alcohol and 5 drops of concentrated H_2SO_4. Heat in the hot-water rack for 10 minutes, and pour into 2 c.c. of Na_2CO_3 solution—characteristic odour of ester (**IV, 35,** *3*) OR, better, indigo test (**IV, 35,** *9*). Mix 15 mg. of the substance with 15 mg. of $CaCO_3$ in a semimicro test-tube, introduce a pressure-filter tube carrying a strip of filter paper moistened with a solution of 5 mg. of *o*-nitrobenzaldehyde in 1 c.c. of NaOH solution. Heat the test-tube strongly. Blue or **green** stain on paper confirms **acetate.**

IX, 6. SPECIAL TESTS FOR MIXTURES OF ACID RADICALS (SEMIMICRO SCALE)

The subject is treated fully in Sections **VIII, 3** and **IV, 44.** All that will be given here concerns the approximate quantities of the reagents to be used on the semimicro scale and any essential experimental modifications ; these are solely for the guidance of the student and need not be followed too closely—

thus the quantities can be considerably reduced, if desired. The special gas-testing apparatus of Fig. 68 will, of necessity, find application here. If the mixture is insoluble in water, the " prepared " solution should be used.

1. Carbonate in the presence of Sulphite.—Treat 20 mg. of the mixture with 20 mg. of finely-powdered $K_2Cr_2O_7$ and 0·5 c.c. of dilute H_2SO_4, place the tube in the hot water rack, and test for CO_2 with lime water (Fig. 68, *c* or *d*).

2. Nitrate in the presence of Nitrite.—Dissolve 20 mg. of the substance in 1 c.c. of water. Remove 1 drop with a glass stirring rod and " spot " on KI-starch paper moistened with very dilute sulphuric acid ; a blue colour is obtained, due to the iodine liberated by the nitrous acid. Add hydrazine sulphate in 10 mg. portions until effervescence ceases. Test for absence of nitrite by " spotting " on KI-starch paper. Then apply the brown ring test for nitrate (Section **IX, 5**).

3. Nitrate in the presence of Bromide and Iodide.—Treat 10–20 mg. of the substance with 1 c.c. of sodium hydroxide solution and 10–20 mg. of Devarda's alloy (or of aluminium as powder or as thin foil), place in the hot water rack, and test for ammonia with red litmus paper and mercurous nitrate paper.

Another procedure is to treat 5 drops of the solution (from 10–20 mg. of the mixture) with ammoniacal silver sulphate reagent until precipitation is complete. Filter off the precipitate, and apply the brown ring test (see *Nitrate* in Section **IX, 5**).

The *ammoniacal silver sulphate reagent* is prepared by dissolving nitrate-free Ag_2SO_4 in the minimum volume of dilute NH_4OH solution. The reagent, $[Ag(NH_3)_2]_2SO_4$, provides a potential high concentration of silver ions in solution.

4. Nitrate in the presence of Chlorate.—Test for nitrate as under 3 ; then acidify with dilute nitric acid, and test for chloride with a few drops of silver nitrate solution.

If chloride is originally present, it may be removed by the addition of saturated silver sulphate solution.

5. Chloride in the presence of Bromide and Iodide.—Dissolve 10–20 mg. of the substance in 0·5–1 c.c. of water in a semimicro boiling tube and add 1–2 c.c. of concentrated nitric acid. Boil gently until the bromine and iodine are volatilised, dilute with 1 c.c. of water, and test for chloride by the addition of a few drops of silver nitrate solution.

6. Chloride in the presence of Iodide (Bromide being absent).—Add excess of silver nitrate solution to 0·5–1 c.c. of the "prepared" solution acidified with dilute nitric acid and filter; reject the filtrate. Wash the precipitate with about 0·5 c.c. of dilute ammonium hydroxide solution and filter again. Acidify the washings with dilute nitric acid: a white precipitate (AgCl) indicates the presence of chloride.

7. Chloride in the presence of Bromide (Iodide being absent).—Acidify 0·5–1 c.c. of the "prepared" solution in a semimicro boiling tube with dilute nitric acid and add an equal volume of concentrated nitric acid. Boil gently until all the bromine is expelled and then add silver nitrate solution. A white precipitate (AgCl) indicates chloride present.

8. Bromide and Iodide in the presence of one another.—Dissolve 10–20 mg. of the substance in 0·5–1 c.c. of water, add 5 drops of dilute sulphuric acid and 0·3–0·5 c.c. of carbon tetrachloride. Add sodium hypochlorite solution dropwise, shaking after the addition of each drop. A violet colouration of the carbon tetrachloride, which appears first, indicates iodide; this subsequently disappears and is replaced by a reddish-brown (or brown) colouration if bromide is present.

9. Phosphate in the presence of Arsenate.—Dissolve 10–20 mg. of the substance in 1 c.c. of water, add 0·5 c.c. of dilute hydrochloric acid, and pass sulphur dioxide for 1–2 minutes. Transfer to a semimicro boiling tube and rinse the test-tube with two 1 c.c. portions of water. Reduce the volume by evaporation to 1 c.c. in order to expel sulphur dioxide completely, transfer back to a semimicro test-tube, pass hydrogen sulphide to completely precipitate the arsenious sulphide, place in the hot water rack for 5 minutes, and filter. Boil off hydrogen sulphide in a semimicro boiling tube, transfer the liquid to a test-tube, and test for phosphate with ammonium molybdate solution and nitric acid.

IX, 7. EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

Preparation of a solution of the solid.—Since the whole scheme for the analysis of cations depends upon the reactions of ions, it is clear that it is first necessary to get the substance into solution. Water is first tried in the cold and then on warming. If insoluble in water, the following reagents are tried as solvents in the order indicated: dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid, concentrated nitric acid, and *aqua regia* (3 volumes of concentrated HCl to 1 volume of concentrated HNO_3). Most substances encountered in an elementary course will dissolve in either water or dilute hydrochloric acid. If concentrated hydrochloric acid has to be used, the solution must be considerably diluted before proceeding with the analysis, otherwise certain cations, such as cadmium and lead, will not be precipitated by hydrogen sulphide. When concentrated nitric acid or *aqua regia* is employed as the solvent, the solution must be evaporated almost to dryness, a little hydrochloric acid added, the solution evaporated again to small bulk, and then diluted with water to dissolve the soluble nitrates (or chlorides). This evaporation is necessary because the nitric acid may react with the hydrogen sulphide subsequently employed in the Group analysis.

To discover the most suitable solvent, treat portions of about 15 mg.* of the finely-powdered substance successively with 0·3–0·5 c.c. of (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid, and (6) *aqua regia* (3 volumes of concentrated HCl : 1 volume of concentrated HNO_3) in the order given. Try the solubility first in the cold and then at the temperature of a boiling water bath for water and dilute hydrochloric acid using a semimicro test-tube. For the other solvents, it will be necessary to investigate the solubility in a semimicro boiling tube; if solution does not take place in the cold, warm gently with a semimicro burner. When all the substance has dissolved, transfer to a semimicro test-tube, rinse the boiling tube with a few drops of water, and add the "rinsings" to the solution. If you are in doubt as to whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass.

If the substance dissolves in water, proceed immediately to the test for the metal ions. If the use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I; the precipitate may either be filtered off and examined for this Group, or else the original substance may be dissolved in dilute nitric acid. If concentrated acids are employed for dissolution, the remarks in the first paragraph must be borne in mind.

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* This is most simply estimated by weighing out 75 mg. and dividing it into 5 approximately equal parts.

When a suitable solvent has been found, the solution for analysis is prepared with about 50 mg. of the solid; the volume of the final solution should be 1–1·5 c.c. This solution is then employed for the Separation of the Metals into Groups according to Table SMI and the resultant precipitates investigated by means of the appropriate Group Separation Table SMII–SMIX.

Before using the Tables, the student should be perfectly clear as to the implied significance of the following terms :—

Filter. *Pressure-filter tube technique.* The pressure-filter tube is packed in the usual manner with either cotton wool or cotton wool-asbestos and the filtrate collected in a semimicro test-tube. The precipitate will, of course, remain on the filter medium. If the filtrate is not perfectly clear, it is returned to the pressure-filter tube and the liquid forced through the filter medium. Washing is readily effected by adding a few drops of the wash liquid to the precipitate and then forcing the liquid through the precipitate by means of a pressure bulb.

Centrifuge technique. The suspension contained in a 3 c.c. centrifuge tube or in a 4 c.c. semimicro test-tube is centrifuged and the supernatant liquid (" centrifugate ") is transferred to another centrifuge or 75 × 10 mm. test-tube by means of a capillary dropper. To wash the precipitate, a few drops of water or wash-liquid are added to the precipitate, the mixture thoroughly stirred, centrifuged, the " centrifugate " removed with a capillary dropper and added to the original filtrate.

Dissolve the precipitate in a solvent. *Pressure-filter tube technique.* This has been fully discussed and illustrated in Section **IX, 1,** but attention is drawn here to a procedure which clearly illustrates one of the outstanding advantages of the use of the pressure-filter tube. A suitable volume (usually 2–3 drops–1 c.c.) is added directly to the precipitate on the cotton wool (or other) medium, the mixture stirred, and the liquid forced through the medium. The filtrate may again be transferred to the pressure-filter tube and the extraction repeated. The operation may, and frequently is, conducted with the filter assembly in the hot water rack.

Centrifuge technique. The precipitate is stirred with a co venient volume (say, up to 1 c.c.) of the solvent for a minu or two, the mixture centrifuged, and the clear liquid remov with a capillary dropper and transferred to another centrifu tube or test-tube by merely compressing the rubber teat. Th dissolution may also be carried out with the centrifuge tu immersed in the hot water rack, and then centrifuged rapidly.

A hint on experimental technique which may prove useful in connexion with those precipitates, particularly from confirmatory tests, which do not settle readily or the colour of which cannot be easily seen in the suspension (*e.g.*, copper ferrocyanide, and the precipitates with aluminon and magneson respectively) is the following. Upon centrifuging, the precipitate usually separates completely and its properties can be readily observed.

Notes to Table SMI. (1) Additions are made with a reagent dropper unless otherwise stated.

(2) If the substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear while hot, but $PbCl_2$ is deposited on cooling the solution, due to the slight solubility of the salt in cold water. Lead may be found in Group II, even if it is not precipitated in Group I.

(3) If arsenates (or dichromates or permanganates) are suspected, pass SO_2 into the solution for 1–2 minutes, and boil off the excess of SO_2 in a semimicro boiling tube. Before passing H_2S, the acidity of the solution should be adjusted. This can be done by either of the following methods.

(*a*) Add 1 drop of methyl violet indicator (0·1% aqueous solution) and introduce dilute HCl dropwise and with constant shaking and stirring until the colour of the solution is yellow-green. The following table gives the colour of the indicator at the various concentrations of acid.

Acid concentration.	*p*H	*Methyl Violet.*
Neutral and alkaline	7 +	Violet
0·1*N* HCl	1·0	Blue
0·25*N* HCl	0·6	Blue-green
0·33*N* HCl	0·5	Yellow-green
0·50*N* HCl	0·3	Yellow

It is recommended that a comparison solution containing, say, 2–3 c.c. of 0·3*N* HCl and 1 drop of indicator be freshly prepared; this will facilitate the correct adjustment of the acidity. A more

Table SMI.—Separation of Metals into Groups

(*Organic Acids, Boric, Hydrofluoric, Silicic and Phosphoric Acids being Absent*)

<table>
<tr><td colspan="6">Add (1) a few drops of dilute HCl to 1–1·5 c.c. of the cold solution. If a ppt. forms, continue adding dilute HCl until no further precipitation takes place. Filter (2).</td></tr>
<tr><td rowspan="5">Residue. The ppt. may contain :—
$PbCl_2$—white.
Hg_2Cl_2—white.
AgCl—white.
Group I (Silver Group) present.
Examine by Group Separation Table SMII.</td><td colspan="5">Filtrate. This must give no precipitate with 1–2 drops of dilute HCl. Adjust the acidity to about 0·3<i>N</i> (3). Pass H_2S through the warm solution until precipitation is complete. Filter.</td></tr>
<tr><td rowspan="4">Residue. The ppt. may contain :—
HgS—black.
PbS—black.
Bi_2S_3—black.*
CuS—black.
CdS—yellow.
SnS—brown.
SnS_2—yellow.
Sb_2S_3—orange.
As_2S_3—yellow
Groups IIA and IIB · (Copper and Arsenic) Groups) present.
Examine by Group Separation Tables SMIII, SMIV and SMV.

* Sometimes dark-brown.</td><td colspan="4">Filtrate. Dilute with one fifth volume of water and pass H_2S again ; add any ppt. which separates to that previously formed (4). Transfer to a semimicro boiling tube and boil off H_2S (test with lead acetate paper). Add 3–5 drops of concentrated HNO_3 and boil to oxidise any ferrous salts to the ferric state (5). The volume at this stage should be about 1 c.c. Transfer to a semimicro test-tube or centrifuge tube. Add 50–100 mg. of solid NH_4Cl or 0·25–0·5 c.c. of 20% NH_4Cl solution, then concentrated NH_4OH solution until a ppt. <i>just</i> appears, then 1 drop of neutral red indicator (6), followed by concentrated NH_4OH solution until the red colour of the indicator changes to yellow and 1–2 drops only in excess. Place the tube in the hot water rack for 5 minutes. Filter (7).</td></tr>
<tr><td rowspan="3">Residue. The ppt. may contain :—
$Fe(OH)_3$—reddish-brown.
$Cr(OH)_3$—green.
$Al(OH)_3$—white.
Possibly MnO_2,H_2O—brown.
Group IIIA (Iron Group) present.
Examine by Group Separation Table SMVI.</td><td colspan="3">Filtrate. Pass H_2S until precipitation is complete. Place in the hot water rack for 2–5 minutes, and filter (7).</td></tr>
<tr><td rowspan="2">Residue. The ppt. may contain :—
CoS—black.
NiS—black.
MnS—pink.
ZnS—white.
Group IIIB (Zinc Group) present.
Examine by Group Separation Table SMVII.</td><td colspan="2">Filtrate. This must give no further ppt. with H_2S (8). Concentrate to about 1 c.c. in a semimicro boiling tube, transfer to a semimicro test-tube, add 10 mg. of solid NH_4Cl or 1 drop of 20% NH_4Cl solution, 1 drop of concentrated NH_4OH solution and about 0·5 c.c. of $(NH_4)_2CO_3$ solution. Place in the hot water rack until ppt. has settled, and add $(NH_4)_2CO_3$ solution until precipitation is complete. Filter (7).</td></tr>
<tr><td>Residue. The ppt. may contain :—
$BaCO_3$—white.
$SrCO_3$—white.
$CaCO_3$—white.
Group IV (Calcium Group present).
Examine by Group Separation Table SMVIII.</td><td>Filtrate. May contain Mg^{++}, Na^+ and K^+ (9). Divide into 2 unequal parts. Evaporate the larger portion to dryness in a 5 c.c. crucible or casserole in the fume cupboard until all ammonium salts are volatilised. White residue.
Group V (Alkali Group) present.
Examine by Group Separation Table SMIX.</td></tr>
</table>

satisfactory standard is a buffer solution prepared by mixing 5 c.c. of *N* sodium acetate and 10 c.c. of *N* HCl; this has a *p*H of 0·5.

(*b*) Use a 10 c.c. conical flask with a file mark to indicate the 5 c.c. level. Transfer the filtrate from Group I to the conical flask, and add concentrated NH_4OH solution by means of a capillary dropper and with constant stirring until the mixture is just alkaline (ignore any precipitate which may separate). Then add dilute HCl dropwise and with vigorous stirring until the mixture is *barely* acid (test with litmus or other indicator paper—see Note 3 to Table SMIII). Now add exactly 0·5 c.c. of 3*N* HCl and dilute the solution to a volume of 5 c.c.

(4) This is really unnecessary if the acidity of the solution has been adequately adjusted. It is, however, a useful precaution for beginners, since CdS, PbS and SnS are incompletely precipitated in the presence of much HCl.

(5) If iron was originally present in the ferric state, it will be reduced to the ferrous state by H_2S. It must be oxidised to the ferric condition to ensure complete precipitation with NH_4Cl and NH_4OH solution. The original solution (or substance) must be tested to determine whether the iron is present in the ferrous or ferric condition.

(6) Alternatively, bromo-thymol blue indicator may be used and concentrated NH_4OH solution added until the solution is just blue. A large excess of NH_4OH solution should be avoided, as this tends to render the precipitate colloidal.

(7) If a pressure-filter tube is used for filtration, a combined cotton wool-asbestos plug is recommended.

(8) If a brown solution or a dark-coloured filtrate is obtained, Ni may be suspected. The dark-coloured solution usually contains colloidal NiS, which runs through a filter medium. In such a case, the solution is either boiled alone in a semimicro boiling tube (adding water, if necessary, to prevent evaporation to dryness) or, better, boiled, after neutralising with acetic acid, until the NiS is coagulated. This may either be added to the Group IIIB precipitate or tested separately for Ni.

(9) It is best to add 1 drop each of $(NH_4)_2SO_4$ solution and $(NH_4)_2C_2O_4$ solution to precipitate any of the Group IV metals which may still be present, removing these by filtration, and then evaporating about two-thirds of the solution to dryness.

Notes to Table SMII. (1) Pressure-filter tube technique: place pressure-filter tube and test-tube in the hot water rack, add 1·5–2 c.c. of hot water, and allow the hot water to pass slowly through the precipitate. Squeeze out the few remaining drops of liquid with the pressure bulb.

Centrifuge tube technique: treat the precipitate with 1 c.c. of

Table SMII.—Analysis of Group I (Silver Group)

<table>
<tr><td colspan="3">Wash the precipitate with 1 c.c. of cold water to which 1 drop of very dilute HCl (0·1<i>N</i>) has been added—reject the washings. Treat the precipitate with 1–2 c.c. of hot water (1) and filter.</td></tr>
<tr><td colspan="2">Residue. May contain Hg_2Cl_2 and AgCl (2). Treat with 0·5 c.c. of dilute NH_4OH solution (3), stir and filter.</td><td rowspan="2">Filtrate. May contain $PbCl_2$.
Add 3 drops of ammonium acetate solution (5) and 1 drop of K_2CrO_4 solution.
Yellow ppt. ($PbCrO_4$).
Lead present.</td></tr>
<tr><td>Residue. Black. $Hg + Hg(NH_2)Cl$.
Mercury present.
Confirm by dissolving ppt. in 5 drops of NaOCl solution and 1 drop of dilute HCl (4).
Add 1–2 drops of $SnCl_2$ solution.
Grey or black confirms mercury.</td><td>Filtrate. May contain $[Ag(NH_3)_2]Cl$.
Add 1 drop of phenolphthalein and acidify with dilute HCl.
White ppt. (AgCl).
Silver present.</td></tr>
</table>

water, place the tube in the hot-water rack, stir the suspension thoroughly, and centrifuge rapidly whilst still hot. Remove the clear liquid with a capillary dropper, and transfer it to another centrifuge tube or 4 c.c. test-tube. If desired, the extraction may be repeated with another 0·5–1 c.c. of water.

(2) If lead has been found, some $PbCl_2$ may still be present. This may be removed by treating the residue with 1 c.c. of hot water as under Note 1, or until the extract no longer gives a precipitate with K_2CrO_4 solution. Reject the washings.

(3) Pressure-filter tube technique: force the NH_4OH solution through the filter and wash with 0·5–1 c.c. of water.

Centrifuge tube technique: stir thoroughly and centrifuge. Transfer to another tube. Repeat with 0·5–1 c.c. of water and combine the solutions.

(4) It is usually necessary to place the tube in the hot-water rack for several minutes in order to dissolve the precipitate completely. Transfer the liquid to a semimicro boiling tube and rinse the tube with about 0·5 c.c. of water. Boil for about 1 minute to expel chlorine, and then apply the $SnCl_2$ test.

(5) The addition of ammonium acetate solution is not essential, but is recommended since the solution is sometimes faintly acid: this reduces the hydrogen ion concentration and thus facilitates the precipitation of the $PbCrO_4$.

IX, 10. Table SMIII.—Analysis of Group II (Copper and Arsenic Groups). Separation of Group IIA (Copper Group) and Group IIB (Arsenic Group)

The ppt. consist of the sulphides of Group IIA metals (HgS, PbS, Bi_2S_3, CuS and CdS) and those of Group IIB (As_2S_3, Sb_2S_3, SnS and SnS_2). Wash the ppt. with 1 c.c. of H_2S water containing 1 drop of NH_4Cl solution (1) and reject the washings. Treat the ppt. with 1·5 c.c. of *yellow* ammonium sulphide solution (2), place in the hot water rack for 1 minute, and filter.

Residue. May contain HgS, PbS, Bi_2S_3, CuS and CdS. Wash once with 1 c.c. of hot water containing 1 drop of NH_4NO_3 solution and reject the washings. **Group IIA present.**	**Filtrate.** May contain solutions of the thio-salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. Acidify with concentrated HCl until acid to litmus paper (3), and place in the hot water rack for 1 minute. A yellow or orange ppt. (4), which may contain As_2S_5 or (As_2S_3), Sb_2S_5 (or Sb_2S_3), SnS_2 and S indicates **Group IIB present.**

Notes to Table SMIII. (1) The H_2S is introduced into the wash liquid to prevent oxidation of the moist sulphides to sulphates; the NH_4Cl (an electrolyte) prevents the sulphides from passing into the colloidal solution.

(2) *Pressure-filter tube technique.* It is recommended that the ammonium sulphide solution be allowed to pass slowly through the precipitate. The filtrate is returned to the pressure-filter tube and the solution allowed to pass through the precipitate again. In all, the precipitate is extracted three times with the solution. The temperature of the water bath should not exceed 50–60° for this operation.

Centrifuge tube technique. Heat in the water bath at 50–60° for 2 minutes with occasional stirring, and centrifuge. Remove the "centrifugate" to another tube with a capillary dropper. Wash the precipitate with 1 c.c. of H_2S water to which 1 drop of NH_4NO_3 solution has been added, and discard the washings.

(3) Place the litmus paper on a dry watch glass. Add the concentrated HCl dropwise to the solution with constant stirring until the moistened rod, when brought into contact with a dry spot on the blue litmus paper, causes the latter to become red. It is inadvisable to place the litmus paper into the solution, because this would give rise to paper shreds and render the solution turbid. This procedure, with obvious modifications, may be used for rendering a solution alkaline.

(4) A white, finely-divided precipitate is sulphur. If the precipitate is white, analysis for Group IIB is omitted.

IX, 11. Table SMIV.—Analysis of Group IIA (Copper Group)

<table>
<tr><td colspan="4">Treat the ppt. with 1–1·5 c.c. of dilute HNO_3, warm (1), and filter.</td></tr>
<tr><td rowspan="3">Residue. Black : HgS. Wash with 1 c.c. of warm water and discard washings. Treat with 5 drops of NaOCl solution and 1 drop of dilute HCl. To the clear solution add 1–2 drops of $SnCl_2$ solution. White ppt. turning grey or black.
Hg(ic) present.</td><td colspan="3">Filtrate. May contain $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$ and $Cd(NO_3)_2$. Add excess of concentrated NH_4OH solution and filter.</td></tr>
<tr><td colspan="2">Residue. May contain $Pb(OH)_2$ and $Bi(OH)_3$. Add 1 c.c. of NaOH solution, place in the hot water rack for 2 minutes, and filter (2)</td><td rowspan="2">Filtrate. May contain $[Cu(NH_3)_4](NO_3)_2$ and $[Cd(NH_3)_4](NO_3)_2$.
If colourless, Cu is absent ; test then directly for Cd (see below) by passing H_2S for 10 seconds into the ammoniacal solution. Yellow ppt. (CdS).
Cd present.
If blue, Cu present.
Divide into 2 unequal parts.
<i>Smaller portion.</i> Acidify with acetic acid and add 1 drop of $K_4[Fe(CN)]_6$ solution. Reddish-brown ppt. on standing for 2–3 minutes.
Cu present.
<i>Larger portion.</i> Add KCN solution dropwise, with stirring until blue colour is discharged, pass H_2S for 30–40 seconds. Yellow ppt. of CdS.
Cd present.</td></tr>
<tr><td>Residue. May be $Bi(OH)_3$. Wash with water and reject washings. Dissolve in 1 c.c. of dilute HCl and add solution to 2 c.c. of sodium stannite reagent (3). White ppt., rapidly turning black.
Bi present.</td><td>Filtrate. May contain sodium plumbite Na_2PbO_2. Acidify with dilute acetic acid, add 1 drop of K_2CrO_4 solution. Yellow ppt. ($PbCrO_4$).
Pb present.</td></tr>
</table>

Notes to Table SMIV. (1) Pressure-filter tube technique: transfer the Group II precipitate and cotton wool to a semimicro boiling tube, add 2 c.c. of dilute HNO_3 and 1 c.c. of water, and boil gently until the sulphides dissolve. Filter through a pressure-filter tube. Treat the residue with NaOCl–HCl, and force the liquid through the filter into a clean test-tube by means of a pressure bulb.

Centrifuge tube technique: treat the precipitate in a centrifuge tube with 1·5 c.c. of dilute HNO_3, place in the hot water rack for 5 minutes, and centrifuge. Remove the "centrifugate" with a capillary dropper to another tube. Wash the residue with 1 c.c. of water, and discard the washings.

(2) Pressure-filter tube technique : the NaOH solution is allowed to pass through the filter, the filtrate returned to the filter tube, and the precipitate extracted a second time.

(3) The *sodium stannite reagent* ($Na_2[SnO_2]$ or $Na_2[Sn(OH)_4]$) is

IX, 12. Table SMV.—Analysis of Group IIB (Arsenic Group)

Add 1 c.c. of concentrated HCl, heat, with stirring, in the hot water rack for 3–5 minutes, and filter.

Residue. May contain As_2S_3. Transfer to a semimicro boiling tube, add 2 c.c. of water and 15–20 mg. of solid $(NH_4)_2CO_3$, and warm gently for 2–3 minutes, Filter, if necessary. Acidify with dilute HCl. Yellow ppt. of As_2S_3. **As present.**	**Filtrate.** May contain $SbCl_3$ (or $H_3[SbCl_6]$) and $SnCl_4$ (or $H_2[SnCl_6]$). Divide into 2 parts. 1. EITHER—Render just alkaline with concentrated NH_4OH solution, add 0·3–0·5 g. of oxalic acid, and pass H_2S. Orange ppt. of Sb_2S_3. **Sb present.** OR—Add 3 drops of 20% $NaNO_2$ solution and 5 drops of rhodamine-B reagent (1). Lavender colour. **Sb present.** 2. Introduce 2 cms. of Fe wire or 20 mg. of Fe filings, and heat in the hot water rack for 5 minutes. Filter and add 2 drops of $HgCl_2$ solution to the filtrate. White, grey or black ppt. **Sn present.**

IX, 13. Table SMVI.—Analysis of Group IIIA (Iron Group)

May contain $Fe(OH_3)$, $Al(OH)_3$, $Cr(OH)_3$ and a little $MnO(OH)_2$ (1). Transfer the ppt. to a semimicro boiling tube containing 2 c.c. of NaOH solution and 0·5 c.c. of 20-volume H_2O_2. Boil gently until the evolution of O_2 ceases. Filter.

Residue. May contain $Fe(OH)_3$ and $MnO(OH)_2$. Dissolve in 0·5 c.c. of dilute HNO_3 and 4 drops of 10-volume H_2O_2 ; warm, if necessary. Divide the solution into 2 parts. 1. Add 1 drop of $K_4[Fe(CN)_6]$ solution. Blue ppt. **Fe present.** 2. Dilute with 1 c.c. of water, boil to decompose any H_2O_2, cool, add 0·5 c.c. of concentrated HNO_3 and 10 mg. of sodium bismuthate, and shake (2). Purple colour of $HMnO_4$. **Mn present.**	**Filtrate.** May contain $NaAlO_2$ and Na_2CrO_4. Divide into 2 parts. 1. Add 1 drop of phenolphthalein, then dilute acetic acid until acid, followed by 1 drop of lead acetate solution. Yellow ppt. of $PbCrO_4$. **Cr present.** 2. Add 1 drop of phenolphthalein, then dilute acetic acid until acid, followed by 2 drops of aluminon reagent and 2 drops of ammonium carbonate solution. Red ppt. **Al present.**

prepared as required by adding NaOH solution dropwise, and with cooling under the tap, to 0·5–1 c.c. of $SnCl_2$ solution until the initial precipitate of $Sn(OH)_2$ dissolves in the excess of NaOH to give a clear (or slightly turbid) solution. The reagent must be freshly prepared because it oxidises in contact with air to sodium stannate and may also decompose spontaneously into sodium stannate ($Na_2[SnO_3]$ or $Na_2[Sn(OH)_6]$) and metallic tin.

Note to Table SMV. (1) It is recommended that a blank composed, of 2 c.c. of dilute HCl, 3 drops of $NaNO_2$ solution and 5 drops of *rhodamine-B reagent* (0·05% aqueous solution) be prepared for comparison.

Notes to Table SMVI. (1) Small quantities of manganese, if present, are often precipitated at this stage, and it is therefore best to test for Mn here.

(2) Alternatively, add 0·5 c.c. of concentrated HNO_3 and 50 mg. of Pb_3O_4. Boil for 1 minute and allow to settle. Purple solution of $HMnO_4$. *Mn present.*

IX, 14. Table SMVII.—Analysis of Group IIIB (Zinc Group)

The ppt. may contain CoS, NiS, MnS, ZnS and finely-divided S. Stir the ppt. in the cold with 1 c.c. of water to which 6 drops of dilute HCl have been added. Filter (1).

<table>
<tr>
<td rowspan="2">Residue. If black, may contain CoS and NiS. Test residue with borax bead.
Blue bead.
Co present.
Add 10–15 drops of dilute HCl and 5 drops of NaOCl solution, stir, and place in the hot water rack for 1–2 minutes. The ppt. dissolves completely. Transfer liquid with the aid of 1 c.c. of water to a semimicro boiling tube, and boil gently to expel Cl_2. Divide the solution into 2 parts.
1. Render alkaline with concentrated NH_4OH solution and add 2 drops of dimethyl glyoxime reagent.
Red ppt.
Ni present.
2. Add 0·5–1 c.c. of amyl alcohol and 50 mg. of solid NH_4CNS, and shake.
Blue colour in the alcohol layer.
Co present.</td>
<td colspan="2">Filtrate. Transfer to a semimicro boiling tube, boil to expel H_2S, return to semimicro test-tube or centrifuge tube, cool, and add excess of NaOH solution. Filter.</td>
</tr>
<tr>
<td>Residue. $Mn(OH)_2$ (often) discoloured), turning brown owing to oxidation. Dissolve in 0·5 c.c. of HNO_3 and 4 drops of 10-volume H_2O_2. Transfer to semimicro boiling tube with 1 c.c. of water and boil to decompose H_2O_2. Cool and add 0·5 c.c. of concentrated HNO_3 and 50 mg. of Pb_3O_4. Boil and allow to stand (2).
Purple solution of $HMnO_4$.
Mn present.</td>
<td>Filtrate. May contain $Na_2[ZnO_2]$. Pass H_2S for not more than 1 minute.
White ppt. of ZnS (3).
Zn present.</td>
</tr>
</table>

Notes to Table SMVII. (1) Pressure-filter tube technique: pass solution through the precipitate on the filter medium three to four times.

(2) Alternatively, add 0·5 c.c. of concentrated HNO_3 and 10 mg. of A.R. sodium bismuthate, stir and allow to settle. Purple solution of $HMnO_4$. *Mn present.*

(3) If the precipitate is white, no further confirmation for Zn is required. If the precipitate is coloured, due largely to CoS, confirm by Rinmann's green test (Section **III, 27,** dry test; footnote to Table XXIV). Alternatively, acidify the alkaline extract with acetic acid (enough sodium acetate is present to buffer the excess

IX, 15. Table SMVIII.—Analysis of Group IV (Calcium Group)

The ppt. may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Treat the ppt. with 1 c.c. of dilute acetic acid and stir. Place in the hot water rack until dissolved. Test 3 drops of the hot solution for barium by adding a drop or two of K_2CrO_4 solution. A yellow ppt. ($BaCrO_4$) indicates *Ba present.*

Ba present.—To the remainder of the hot solution, add a slight excess of K_2CrO_4 solution (*i.e.*, until the solution just assumes an orange tint), and filter the $BaCrO_4$ (*C*). Render the filtrate alkaline with NH_4OH solution and add excess of $(NH_4)_2CO_3$ solution. Place the tube in the hot water rack. A white ppt. indicates the presence of $SrCO_3$ and/or $CaCO_3$. Filter the ppt., and wash with a little hot water. Dissolve the ppt. in 1 c.c. of dilute acetic acid, place in the hot water rack, and remove the excess of CO_2 by a stream of air (produced with a large dropper by alternately depressing and releasing the rubber teat whilst the dropper is immersed in and withdrawn from the solution) (solution *A*).

Ba absent.—Throw away the portion used for testing for barium, and employ the remainder of the hot solution (*B*), after the CO_2 has been expelled by a stream of air from a large dropper, in testing for Sr and Ca.

Residue (*C*). Yellow: $BaCrO_4$. Wash with hot water. Dissolve in a few drops of concentrated HCl, evaporate to dryness in a 5 c.c. crucible, and apply the flame test. Green flame. **Ba present.**	**Filtrate.** Use acetic acid solutions *A* or *B*. Divide into 2 equal parts. 1. Render alkaline with NH_4OH solution add 2 c.c. of boiling, saturated $(NH_4)_2SO_4$ solution and place in the hot water rack for 5 minutes. White ppt. **Sr present.** Confirm thus: filter off the ppt.; stir the ppt. with 3–4 drops of water and transfer by means of capillary dropper to 1 square cm. of quantitative filter paper contained in a 5 c.c. crucible. Ignite until the paper has charred, add 1–2 drops of concentrated HCl, and apply flame test. Crimson flame (1). **Sr present.** 2. Add solid NH_4Cl to the cold solution until almost saturated, then 5 drops of $K_4[Fe(CN)_6]$ solution, and allow to stand for 5 minutes. Pale yellow ppt. **Ca present.**

of acid), and pass H_2S for several seconds. A white precipitate confirms Zn. Cobalt sulphide is not precipitated under these conditions.

Note to Table SMVIII. (1) If Ca is present in considerable excess, the brick-red Ca flame will appear first, followed by the crimson Sr flame. If Sr is absent, no precipitate is obtained with $(NH_4)_2SO_4$ solution under the above experimental conditions.

IX, 16. Table SMIX. Analysis of Group V (Alkali Group).

Smaller portion of Group IV Filtrate	*Residue from larger portion of Group IV Filtrate*
Add 2 drops of Na_2HPO_4 solution and place in the hot water rack for 5–10 minutes. White crystalline ppt. of $Mg(NH_4)PO_4$. **Mg present.** *Confirmatory test.* Dissolve ppt. in 1 c.c. of dilute HCl, add 1 drop of magneson reagent, followed by NaOH solution until alkaline. A blue *ppt.* confirms Mg.	Add 1 c.c. of water, stir, filter if necessary, and divide the solution into 2 parts. 1. Add 10 mg. of A.R. $Na_3[Co(NO_2)_6]$, shake until dissolved, then add 1 c.c. of alcohol. Allow to stand for 3 minutes. Yellow ppt. **K present.** Apply flame test, using two thicknesses of cobalt glass ; crimson flame. 2. Add 10 drops of magnesium uranyl acetate reagent, stir, and allow to stand for 3 minutes. Yellow crystalline ppt. **Na present.** Apply flame test ; persistent yellow flame.

With the experience gained in the foregoing elementary analyses, the student should have no difficulty in adapting the macro procedures of more advanced analysis described elsewhere in this volume to the semimicro scale. As an example we may take the Phosphate Separation Table (compare Section **V, 7,** Table XXV and Section **VI, 2**) ; this is given on the next page (Table SMX).

Note to Table SMX. (1) The bench reagent usually contains excess of free acid added during its preparation in order to produce a clear solution ; this may prevent the precipitation of the basic acetate on boiling and hence the excess of ferric iron will not be completely removed from solution. It is recommended that Na_2CO_3 solution be added to 1 c.c. of the side-shelf $FeCl_3$ reagent until a slight precipitate forms, this is filtered off and the filtrate employed.

IX, 17. Table SMX.—Phosphate Separation Table.

Boil the filtrate from Group II in a semimicro boiling tube to remove H_2S, then add 5 drops of concentrated HNO_3 and boil for 1 minute. Transfer to a semimicro test-tube. Add 50–100 mg. of solid NH_4Cl or 0·25–0·50 c.c. of 20% NH_4Cl solution, then concentrated NH_4OH solution until a ppt. *just* appears, 1 drop of neutral red indicator, followed by concentrated NH_4OH solution until the red colour of the indicator changes to yellow and 1 drop in excess. Place the tube in the hot water rack for 5 minutes. Filter and wash with 1 c.c. of water to which 1 drop of concentrated NH_4Cl solution has been added.

Residue. May contain hydroxides of Group IIIA and phosphates of Groups IIIA, IIIB and IV metals and of Mg. Transfer to a semimicro boiling tube, add 2 c.c. of NaOH solution and 0·5 c.c. of 10-volume H_2O_2. Boil until evolution of O_2 ceases, and filter.

Residue. Dissolve in 0·5 c.c. of dilute HNO_3 and 4 drops of 10-volume H_2O_2; dilute to 1 c.c.

Remove 2 drops, add 4 drops of concentrated HNO_3 and 4 drops of ammonium molybdate reagent, place in the hot water rack at 40–60° for 5 minutes.

Yellow ppt.

Phosphate present.

Remove 2 drops, add 1 drop of $K_4[Fe(CN)_6]$ solution.

Blue ppt.

Fe present.

To remainder of the solution, add 1 drop of methyl red, and dilute NH_4OH solution until the mixture is just yellow. Add 2 drops of dilute acetic acid and 20–30 mg. of solid ammonium acetate. Add 2 or sufficient drops of "neutral" $FeCl_3$ solution (1) until the mixture is just red (thus ensuring sufficient Fe^{+++} to ppt. all PO_4^{---} as $FePO_4$), place in the hot water rack for 10 minutes, and filter.

Residue. $FePO_4$ and some basic ferric acetate. Reject.

Filtrate. Combine with *A*, transfer to a semimicro boiling tube, evaporate to 1 c.c. and return to a semimicro test-tube. Add 20 mg. of solid NH_4Cl or 0·1 c.c. of 20% NH_4Cl solution and NH_4OH solution in slight excess. Place in the hot water rack for 5 minutes. Filter, if necessary.

Residue. Examine for Al and Cr (and Mn) if not previously tested for (Table SMVI).

Filtrate. Examine for Groups IIIB to V in the usual manner.

Filtrate. May contain $NaAlO_2$ and Na_2CrO_4. Test for Al and Cr according to Table SMVI.

Filtrate (*A*)

Oxides, Hydroxides, Free Metals, and Simple Alloys.—If a solid substance is found to contain no anions, it may be an oxide, or hydroxide, or a metal or a mixture of metals, or an alloy. Metals and alloys have certain characteristic physical properties; many metals evolve hydrogen on treatment with dilute acids. As a rule, nitric acid must be employed as solvent, and it will then be necessary to remove the excess of nitric acid (as already described above) before proceeding to the Group analysis.

IX, 18. ANALYSIS OF A LIQUID

If a liquid is supplied for analysis, proceed as follows:—

(1) Observe the colour, odour and any special physical properties.

(2) Test its reaction to litmus (or equivalent test) paper.

(*a*) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.

(*b*) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, sulphides, hypochlorites and peroxides of the alkali metals, *etc.*

(*c*) *The solution reacts acid*: this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to a solution of salts in acids.

(3) Evaporate a portion of the liquid to dryness on the water bath (use a 3 or 5 c.c. crucible and stand it over one of the openings in the hot water rack); carefully smell the vapours evolved from time to time. If a solid residue remains, examine it as detailed above for a solid substance. If a liquid remains, evaporate cautiously on a wire gauze in the fume chamber; a solid residue should then be examined in the usual way. If no residue is obtained, the original liquid consists of some volatile substances which may be water or water containing certain gases or volatile substances, such as CO_2, NH_3, SO_2, H_2S, HCl, HBr, HI, H_2O_2 or $(NH_4)_2CO_3$, all of which can be readily detected by special tests. It is best to neutralise with sodium carbonate and test for acid radicals (anions).

IX, 19. APPARATUS FOR SEMIMICRO QUALITATIVE ANALYSIS

The liquid and solid reagents recommended for each student are detailed in Section **IX, 1**; the necessary side-shelf reagents may be selected from those given in the Appendix (Section **A,** 2). The apparatus suggested for each student is listed below (see plate, Fig. 70).

Pressure-Bulb Technique

1 Rubber pressure-bulb (Fig. 57) (that from a 3 or 4-ounce rectum syringe is satisfactory).
2 Small rubber bungs, one to fit the pressure-bulb and the other to fit a pressure-filter tube.
1 Clamp and stand (for pressure-bulb).
1 Wooden block, single hole, for semimicro test-tube.
1 Bottle (30 c.c., w.m.) filled with cotton wool.
1 Bottle (30 c.c., w.m.) for " Gooch " asbestos.
12 Semimicro test-tubes (100 × 12 mm., Pyrex).
1 Semimicro test-tube rack.
3 Semimicro boiling tubes (60 × 25 mm., Pyrex).
1 Wooden block for boiling tubes.
3 Test-tubes, 150 × 18 mm. (to hold droppers, etc.), and wooden stand.
6 Droppers,* ocmplete with rubber teats (Fig. 51, *a* and *b*).
1 Large dropper (125 × 8 mm.).
2 Stirring rods with bulb end (Fig. 50, *c*) ; otherwise as in Fig. 50, *a* or *b*.*
1 Drawn-out rod for removing filter plugs from pressure-filter tubes ; * alternatively, 1 equivalent nichrome or monel metal wire.
3 Pressure-filter tubes.
2 Graduated pipettes, 2 c.c.
1 250 c.c. beaker (Pyrex).
1 Hot water rack (Fig. 61).
1 Bunsen burner.
2 Tripods and 2 gauzes.
1 Semimicro burner.
1 Semimicro spatula (Fig. 60).
2 Crucibles, 5 c.c.
2 Conical flasks, 10 c.c. (Pyrex).
1 Conical flask, 25 c.c. (Pyrex).
2 Beakers, 10 c.c. (Pyrex).
1 Watch glass.
1 Packet blue litmus paper.
1 Packet red litmus paper.
1 Semimicro test-tube holder (Fig. 63).
1 Semimicro test-tube brush (Fig. 66).
1 Platinum wire (5 cm. of 0·3 mm. diameter).
1 Spot plate.

* To be constructed by the student from the glass tubing and rod supplied.

1 Wash-bottle, 100 c.c., provided with fine jet; * alternatively, 1 n.m. bottle, 30 or 60 c.c., fitted with reagent dropper (for distilled water).
1 Large wash-bottle, 250 or 500 c.c.*
1 Triangular file.
1 Crucible tongs.
1 Wire triangle.

Additional Apparatus for Centrifuge Technique

1 Hand semimicro centrifuge and cover (to be shared by 6 students); alternatively, an electrically driven semimicro centrifuge may be used.
3 Semimicro test-tubes (75 × 10 mm., Pyrex).†
6 Semimicro centrifuge tubes (3 c.c., Pyrex).†
3 Pressure-filter tubes to fit 75 × 10 mm. test-tubes.
1 Wooden rack for semimicro test-tubes and centrifuge tubes.

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* To be constructed by the student from the flask and glass tubing provided.

† These replace 9 of the 100 × 12 mm. test-tubes required in the pressure-bulb technique, if the centrifuge technique is adopted.

APPENDIX

A, 1. ATOMIC WEIGHTS OF ELEMENTS (1937)

Aluminium Al	26·97	Manganese Mn	54·93
Antimony Sb	121·76	Mercury Hg	200·61
Argon A	39·94	Molybdenum Mo	96·0
Arsenic As	74·91	Nickel Ni	58·69
Barium Ba	137·36	Nitrogen N	14·01
Beryllium Be	9·02	Oxygen O	16·000
Bismuth Bi	209·00	Palladium Pd	106·7
Boron B	10·82	Phosphorus P	31·02
Bromine Br	79·92	Platinum Pt	195·23
Cadmium Cd	112·41	Potassium K	39·10
Calcium Ca	40·08	Radium Ra	226·05
Carbon C	12·01	Selenium Se	78·96
Cerium Ce	140·13	Silicon Si	28·06
Chlorine Cl	35·46	Silver Ag	107·88
Chromium Cr	52·01	Sodium Na	23·00
Cobalt Co	58·94	Strontium Sr	87·63
Copper Cu	63·57	Sulphur S	32·06
Fluorine F	19·00	Tellurium Te	127·61
Germanium Ge	72·60	Thallium Tl	204·39
Gold Au	197·2	Thorium Th	232·12
Helium He	4·00	Tin Sn	118·70
Hydrogen H	1·008	Titanium Ti	47·90
Iodine I	126·92	Tungsten W	184·0
Iron Fe	55·84	Uranium U	238·07
Lead Pb	207·21	Vanadium V	50·95
Lithium Li	6·94	Zinc Zn	65·38
Magnesium Mg	24·32	Zirconium Zr	91·22

A, 2. REAGENTS

CONCENTRATED ACIDS

	Specific Gravity	*Per cent. by Weight*	*Approximate Normality*
Acetic acid, glacial	1·05	99·5	17*N*
Hydrochloric acid	1·19	37·9	12*N*
Nitric acid	1·42	69·8	16*N*
Perchloric acid		60	9*N*
Phosphoric acid	1·7	85	15*N*
Sulphuric acid	1·84	96·0	36*N*

DILUTED ACIDS

	Approximate Normality
Acetic acid.—Dilute 285 c.c. of the concentrated acid to 1 litre with water	5N
Hydrochloric acid.—Dilute 430 c.c. of the concentrated acid to 1 litre with water	5N
Nitric acid.—Dilute 310 c.c. of the concentrated acid to 1 litre with water	5N
Sulphuric acid.—Pour 140 c.c. of the concencentrated acid slowly and with constant stirring into 500 c.c. of water, cool, and dilute to 1 litre	5N
Sulphurous acid.—Prepare a saturated solution in water	0·3N

BASES

Ammonium hydroxide solution, concentrated.—The commercial product, sp. gr. 0·88, contains about 28% NH_3	15N
Ammonium hydroxide solution, dilute.—Dilute 335 c.c. of the concentrated solution to 1 litre with water	5N
Barium hydroxide solution.—Shake 70 grams of crystallised barium hydroxide $Ba(OH)_2,8H_2O$ with 1 litre of water ; filter or siphon off the liquid (saturated solution) and protect from CO_2 of the air	0·4N
Calcium hydroxide solution.—Shake 2–3 grams of calcium hydroxide with 1 litre of water ; filter or siphon off the liquid (saturated solution) and protect from CO_2 of the air	0·04N
Potassium hydroxide solution.—Dissolve 310 grams of the ordinary " pure " sticks (about 90% KOH) in water and dilute to 1 litre	5N
Sodium hydroxide solution.—Dissolve 220 grams of the ordinary " pure " sticks (about 90% NaOH) in water and dilute to 1 litre	5N

SALT SOLUTIONS *

	Approximate Normality
Ammonium acetate, $NH_4.C_2H_3O_2$ (M.W. 77).—Dissolve 231 grams of the salt in 1 litre of water	3*N*
Ammonium carbonate (the commercial salt is a mixture of NH_4HCO_3 and $NH_4CO_2NH_2$).—Dissolve 160 grams of the salt in a mixture of 140 c.c. of conc. ammonium hydroxide solution and 860 c.c. of water	4*N*
Ammonium chloride, NH_4Cl (M.W. 53·5).—Dissolve 270 grams of the salt in 1 litre of water ...	5*N*
Ammonium oxalate, $(NH_4)_2C_2O_4,H_2O$ (M.W. 142).—Dissolve 35 grams of the crystalline salt in 1 litre of water	0·5*N*
Ammonium sulphate, $(NH_4)_2SO_4$ (M.W. 132).—Dissolve 132 grams of the salt in 1 litre of water	2*N*
Yellow ammonium sulphide solution, $(NH_4)_2S_x$.—Use the solution available commercially. It may be prepared, if desired, as follows. Saturate 200 c.c. of conc. ammonia solution with H_2S, keeping the solution cold; add 10 grams of flowers of sulphur and 200 c.c. of conc. ammonia solution, shake until the sulphur has dissolved, and dilute to 1 litre.	6*N*
Colourless ammonium sulphide solution $(NH_4)_2S$.—Saturate 2 parts by volume of conc. ammonia solution with H_2S, keeping the solution cold, add an equal volume of conc. ammonia solution and dilute with 6 parts of water. This solution is prepared as required.	6*N*
Barium chloride, $BaCl_2,2H_2O$ (M.W. 244).—Dissolve 61 grams of the salt in 1 litre of water ...	0·5*N*
Bromine water, Br_2 (M.W. 160).—A saturated aqueous solution is prepared by shaking 35 grams or 11 c.c. of liquid bromine with water.	
Calcium chloride, $CaCl_2,6H_2O$ (M.W. 219).—Dissolve 55 grams of the hydrated salt in 1 litre of water	0·5*N*
Calcium sulphate, $CaSO_4,2H_2O$ (M.W. 172).—Shake 3 grams of the salt with 1 litre of water; filter or decant the saturated solution after several hours	0·03*N*

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* The common reagents chlorine water, bromine water, iodine solution, and hydrogen sulphide water are included here.

	Approximate Normality
Chlorine water, Cl_2 (M.W. 71).—Saturate 250 c.c. of water with chlorine. The chlorine may be generated by dropping conc. HCl upon $KMnO_4$. Preserve in a dark-coloured bottle. The solution contains 6·5 grams of Cl_2 per litre.	
Cobalt nitrate, $Co(NO_3)_2,6H_2O$ (M.W. 291).—Dissolve 44 grams of the salt in 1 litre of water ...	0·3*N*
Copper sulphate, $CuSO_4,5H_2O$ (M.W. 249·5).—Dissolve 125 grams of the salt in 1 litre of water containing 10 c.c. of dilute sulphuric acid... ...	0·5*N* (as oxidant)
Ferric chloride, $FeCl_3,6H_2O$ (M.W. 270).—Dissolve 135 grams of the hydrated salt in 1 litre of water containing 20 c.c. of conc. HCl	0·5*N* (as oxidant)
Ferrous sulphate, $FeSO_4,7H_2O$ (M.W. 277).—Dissolve 140 grams of the salt in 1 litre of water containing 7 c.c. of conc. H_2SO_4	0·5*N* (as reductant)
Hydrogen sulphide solution, H_2S (M.W. 34).—Saturate 250 c.c. of water with H_2S gas derived from a Kipp's apparatus. The solution contains approximately 4·2 grams of H_2S per litre. ...	0·05*N*
Iodine solution, I_2 (M.W. 254).—Dissolve 12·7 grams of iodine in a solution of 20 grams of pure KI in 30 c.c. of water, and dilute to 1 litre with water	0·1*N*
Lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$ (M.W. 379).—Dissolve 95 grams of the salt in 1 litre of water ...	0·5*N*
Magnesium sulphate, $MgSO_4,7H_2O$ (M.W. 246).—Dissolve 62 grams of the salt in 1 litre of water ...	0·5*N*
Mercuric chloride, $HgCl_2$ (M.W. 272).—Dissolve 27 grams of the salt in 1 litre of water	0·2*N*
Potassium chromate, K_2CrO_4 (M.W. 194).—Dissolve 49 grams of the salt in 1 litre of water ...	0·5*N* (as precipitant)
Potassium cyanide, KCN (M.W. 65).—Dissolve 32·5 grams of the salt in 1 litre of water	0·5*N*
Potassium ferricyanide, $K_3[Fe(CN)_6]$ (M.W. 329).—Dissolve 55 grams of the salt in 1 litre of water	0·5*N* (as precipitant)
Potassium ferrocyanide, $K_4[Fe(CN)_6],3H_2O$ (M.W. 422).—Dissolve 53 grams of the salt in 1 litre of water*	0·5*N* (as precipitant)

* The reagent employed to remove Ca is 2*N* (Section **III, 27**, *6*).

	Approximate Normality
Potassium iodide, KI (M.W. 166).—Dissolve 83 grams of the salt in 1 litre of water—	0·5*N*
Potassium permanganate, $KMnO_4$ (M.W. 316).—Dissolve 3·2 grams of the salt in 1 litre of water; filter through glass wool	0·1*N* (as oxidant)
Potassium thiocyanate, KCNS (M.W. 97).—Dissolve 49 grams of the salt in 1 litre of water	0·5*N*
Silver nitrate, $AgNO_3$ (M.W. 170).—Dissolve 17 grams of the salt in 1 litre of water	0·1*N*
Silver sulphate, Ag_2SO_4 (M.W. 312).—Dissolve 8 grams of the salt in 1 litre of water. This is nearly a saturated solution	0·05*N*
Sodium acetate, $Na.C_2H_3O_2,3H_2O$ (M.W. 136).—Dissolve 408 grams of the crystallised salt in 1 litre of water	3*N*
Sodium carbonate, $Na_2CO_3,10H_2O$ (M.W. 286).—Dissolve 430 grams of the crystallised salt in 1 litre of water	3*N*
Disodium hydrogen phosphate, $Na_2HPO_4,12H_2O$ (M.W. 358).—Dissolve 120 grams of the salt in 1 litre of water	*N*
Stannous chloride, $SnCl_2,2H_2O$ (M.W. 226).—Dissolve 56 grams of the salt in 100 c.c. of conc. HCl and dilute to 1 litre. Keep a few pieces of tin in the bottle to prevent oxidation	0·5*N*

SPECIAL REAGENTS

Details for the preparation of most of the special, largely organic, reagents are given in the text; these can be readily found by reference to the Index. Those that are required for macro-qualitative analysis and have not been described in the text are collected here.

Ammonium molybdate reagent.—*Method A.* Dissolve 50 grams of the commercial salt $(NH_4)_6Mo_7O_{24},4H_2O$ (a para-molybdate) or 40 grams of pure molybdenum trioxide MoO_3 in a mixture of 70 c.c. of conc. ammonia solution and 140 c.c. of water; when solution is complete, add very slowly and with vigorous stirring to a mixture of 250 c.c. of conc. HNO_3 and 500 c.c. of water; dilute to 1 litre. Allow to stand 1–2 days and decant the clear solution.

Method B. Dissolve 45 grams of pure commercial ammonium molybdate in a mixture of 40 c.c. of conc. ammonia solution and 60 c.c. of water, add 120 grams of ammonium nitrate, and dilute to 1 litre with water.

Fehling's solution.—*Solution A* (blue): dissolve 34·6 grams of pure $CuSO_4,5H_2O$ in distilled water and dilute to 500 c.c.

Solution B (colourless): dissolve 175 grams of sodium potassium tartrate (Rochelle salt) and 70 grams of pure NaOH in water, and dilute to 500 c.c. (alternatively, one may dissolve 121 grams of pure NaOH and 93·1 grams of pure tartaric acid in water, and then dilute the solution to 500 c.c.).

Formaldehyde.—Dilute the commercial 40% solution (1 part) with water (7 parts).

Hydrogen peroxide.—Use the commercial "10-volume" or 3% solution unless otherwise stated.

Indigo solution.—Gently warm 1 gram of indigo with 12 c.c. of conc. H_2SO_4, allow to stand for 48 hours, and pour into 240 c.c. of water. Filter.

Magnesia mixture.—Dissolve 55 grams of $MgCl_2,2H_2O$ and 135 grams of NH_4Cl in water, add 350 c.c. of conc. ammonia solution, and dilute to 1 litre.

Sodium cobaltinitrite solution.—Dissolve 17 grams of the *pure* (*e.g.* analytical reagent quality) salt $Na_3[Co(NO_2)_6]$ in 250 c.c. of water. Alternatively, the solution may be prepared as follows:—dissolve 12 grams of $Co(NO_3)_2,6H_2O$ in 30 c.c. of water; dissolve 20 grams of $NaNO_2$ in 30 c.c. of water; mix the two solutions with vigorous stirring and add 5 c.c. of glacial acetic acid, shake well, dilute to 250 c.c., allow to stand for a few days and filter. The solution should not be kept for more than a few weeks as it is somewhat unstable.

Sodium nitroprusside solution.—Prepare a solution as required by dissolving a crystal (about the size of a pea) in 5 c.c. of water.

Starch solution.—Triturate 0·5 gram of soluble starch with a little cold water into a thin paste and add 25 c.c. of boiling water. Boil until a clear solution is obtained (5 minutes). This solution should be freshly prepared as required. A more stable starch solution is obtained by adding 0·5 gram of KI and 2–3 drops of chloroform.

SOLVENTS

Amyl alcohol, $C_5H_{11}OH$
Carbon disulphide, CS_2
Carbon tetrachloride, CCl_4
Chloroform, $CHCl_3$
Ethyl alcohol (rectified spirit; 95%), C_2H_5OH
Methyl alcohol (acetone free), CH_3OH
Ethyl ether, $(C_2H_5)_2O$

SOLID REAGENTS

Aluminium (turnings or foil), Al
Ammonium chloride, NH_4Cl
Ammonium nitrate, NH_4NO_3
Ammonium thiocyanate, NH_4CNS
Asbestos fibre, for filters
Borax, $Na_2B_4O_7,10H_2O$
Calcium chloride, $CaCl_2$
Calcium fluoride, CaF_2
Copper (foil or turnings), Cu
Devarda's alloy (powder)
Ferrous sulphate, $FeSO_4,7H_2O$
Fusion mixture, $Na_2CO_3 + K_2CO_3$
Glass wool
Iron (wire or powder), Fe
Lead dioxide (Mn free), PbO_2
Litmus paper (red and blue)
Manganese dioxide (precipitated)
Microcosmic salt, $Na(NH_4)HPO_4,4H_2O$
Potassium bisulphate, $KHSO_4$
Potassium carbonate, K_2CO_3
Potassium chlorate, $KClO_3$
Potassium cyanide, KCN
Potassium dichromate, $K_2Cr_2O_7$
Potassium nitrate, KNO_3
Potassium nitrite, KNO_2
Potassium iodide, KI
Potassium permanganate, $KMnO_4$
Potassium persulphate, $K_2S_2O_8$
Silica (precipitated), SiO_2
Sodium acetate (fused), $Na.C_2H_3O_2$
Sodium bicarbonate, $NaHCO_3$
Sodium bismuthate, $NaBiO_3$
Sodium bitartrate, $NaH.C_4H_4O_6$
Sodium hydroxide, NaOH
Sodium nitrite, $NaNO_2$
Sodium nitroprusside, $Na_2[Fe(CN)_5NO],2H_2O$
Sodium sulphite, $Na_2SO_3,7H_2O$
Stannic chloride, $SnCl_4,5H_2O$
Stannous chloride, $SnCl_2,2H_2O$
Starch (soluble)
Starch-iodide paper
Sulphur (flowers), S
Tartaric acid, $H_2.C_4H_4O_6$
Tin (pure foil), Sn
Turmeric paper
Zinc (20 mesh) Zn

A, 3. TEST SOLUTIONS

In order that the student may be able to judge the relative proportions of the constituents of mixtures from the size of precipitates, it is essential that he employs solutions of known strengths from the very outset. The test solutions described below contain 10 milligrams of the cation or anion per c.c. If desired, stock solutions containing 100 milligrams per c.c. may be prepared (provided the solubility of the salt is sufficiently high) and these subsequently diluted. *Pure* chemicals should be employed for the preparation of these solutions.

The cations are arranged in the order of the Groups; the anions in the order in which they are described in Chapter IV.

CATIONS

Cation	*Formula of dry salt*	*Grams of salt per litre of solution*	*Special precautions in preparation of the solution*
Hg_2^{++}(ous)	$Hg_2(NO_3)_2.2H_2O$	14·0	Use 100 c.c. of dilute HNO_3.
Ag^+	$AgNO_3$	15·8	
Pb^{++}	$Pb(NO_3)_2$	16·0	Use 5 c.c. of dilute HNO_3.
	or $Pb(C_2H_3O_2)_2$, $3H_2O$	18·3	Use 5 c.c. of dilute $H.C_2H_3O_2$
Hg^{++}(ic)	$HgCl_2$	13·5	
Bi^{+++}	$Bi(NO_3)_3,5H_2O$	23·2	Dissolve salt in 100 c.c. of dilute HNO_3 and dilute to 1 litre.
Cu^{++}	$CuSO_4,5H_2O$	39·3	Use 5 c.c. of dilute H_2SO_4.
	or $CuCl_2,2H_2O$	26·8	Use 5 c.c. of dilute HCl.
Cd^{++}	$3CdSO_4,8H_2O$	22·8	Use 5 c.c. of dilute H_2SO_4.
	or $Cd(NO_3)_2,4H_2O$	27·8	Use 5 c.c. of dilute HNO_3.
As (ous)	As_2O_3	13·2	Dissolve in hot water containing 20 c.c. of dilute HCl and dilute to 1 litre.
As (ic)	As_2O_5	15·3	As for arsenious compound.
	or Na_2HAsO_4, $12H_2O$	53·7	
Sb (ous)	$SbCl_3$	18·8	Dissolve in 500 c.c. of dilute HCl and dilute to 1 litre.
Sb (ic)	$SbCl_5$	24·5	As for antimonious compound.
Sn^{++}(ous)	$SnCl_2,2H_2O$	19·0	Dissolve in 100 c.c. of conc. HCl and dilute to 1 litre.
Sn^{++++}(ic)	$SnCl_4,5H_2O$	29·5	Dissolve in 500 c.c. of dilute HCl and dilute to 1 litre.
Fe^{++}(ous)	$FeSO_4,(NH_4)_2SO_4$, $6H_2O$	70·3	Use 20 c.c. of dilute H_2SO_4.
Fe^{+++}(ic)	$FeCl_3,6H_2O$	48·4	Use 50 c.c. of dilute HCl.
Cr^{+++}	$CrCl_3,6H_2O$	51·2	Use 50 c.c. of dilute HCl.
	or K_2SO_4, $Cr_2(SO_4)_3,24H_2O$	96·0	Use 50 c.c. of dilute H_2SO_4.
Al^{+++}	$Al_2(SO_4)_3,18H_2O$	123·5	Use 20 c.c. of dilute H_2SO_4.
	or $K_2SO_4,Al_2(SO_4)_3$, $24H_2O$	175·9	Use 20 c.c. of dilute H_2SO_4.
Co^{++}	$Co(NO_3)_2,6H_2O$	49·4	
Ni^{++}	$NiSO_4,7H_2O$	47·8	
	or $NiCl_2,6H_2O$	40·5	
Mn^{++}	$MnSO_4,4H_2O$	40·7	
	or $MnCl_2,4H_2O$	36·0	
Zn^{++}	$ZnSO_4,7H_2O$	44·0	
	or $Zn(NO_3)_2$	29·0	
Ba^{++}	$BaCl_2,2H_2O$	17·8	
	or $Ba(NO_3)_2$	19·0	
Sr^{++}	$SrCl_2,6H_2O$	30·4	
	or $Sr(NO_3)_2$	24·2	
Ca^{++}	$CaCl_2,2H_2O$	36·7	
	or $Ca(NO_3)_2,4H_2O$	58·9	

Cations (contd.)

Cation	*Formula of dry salt*	*Grams of salt per litre of solution*	*Special precautions in preparation of the solution*
Mg^{++}	$MgSO_4,7H_2O$	101·4	
	or $Mg(NO_3)_2,6H_2O$	105·4	
K^+	KCl	19·1	
	or KNO_3	25·9	
Na^+	$NaCl$	25·4	
	or $NaNO_3$	37·0	
NH_4^+	NH_4Cl	29·7	
	or NH_4NO_3	44·4	

Note. If a slightly turbid solution is obtained with the cations of Groups IIIB, IV and Mg, about 5 c.c. per litre of the dilute acid, corresponding to the anion of the salt, should be added.

ANIONS

Anion	*Formula of salt*	*Grams of salt per litre of solution*
CO_3^{--}	$Na_2CO_3,10H_2O$	49·3
SO_3^{--}	$Na_2SO_3,7H_2O$ *	31·5
$S_2O_3^{--}$	$Na_2S_2O_3,5H_2O$ *	22·2
S^{--}	$Na_2S,9H_2O$	75·1
NO_2^-	$NaNO_2$*	15·0
CN^-	KCN	25·0
CNO^-	$KCNO$	19·3
CNS^-	$KCNS$	16·9
$[Fe(CN)_6]^{----}$	$K_4[Fe(CN)_6],3H_2O$	19·9
$[Fe(CN)_6]^{---}$	$K_3[Fe(CN)_6]$	15·5
Cl^-	$NaCl$	16·5
Br^-	KBr	14·9
I^-	KI	13·1
F^-	NaF	22·1
NO_3^-	$NaNO_3$	13·7
ClO_3^-	$KClO_3$	14·7
BrO_3^-	$KBrO_3$	13·1
IO_3^-	KIO_3	12·2
ClO_4^-	$KClO_4$	12·3
BO_2^- (borate)	$Na_2B_4O_7,10H_2O$	22·5
SO_4^{--}	$Na_2SO_4,10H_2O$	33·6
SiO_3^{--}	Na_2SiO_3	16·1
$[SiF_6]^{--}$ (silicofluoride)	$Na_2[SiF_6]$	13·2
PO_4^{---}	$Na_2HPO_4,12H_2O$	37·7
HPO_3^{--} (phosphite)	$Na_2HPO_3,2H_2O$	27·0
$H_2PO_2^-$ (hypophosphite)	NaH_2PO_2,H_2O	16·3
CrO_4^{--}	K_2CrO_4	16·7
MnO_4^-	$KMnO_4$	13·3
$C_2H_3O_2^-$ (acetate)	$Na.C_2H_3O_2,3H_2O$	23·1
$H.CO_2^-$ (formate)	$H.CO_2Na$	13·5
$C_2O_4^{--}$ (oxalate)	$Na_2.C_2O_4$	15·2
$C_4H_4O_6^{--}$ (tartrate)	$NaK.C_4H_4O_6,4H_2O$	19·1
$C_6H_5O_7^{---}$ (citrate)	$Na_3.C_6H_5O_7,2H_2O$	15·6
$C_7H_5O_3^-$ (salicylate)	$C_6H_4(OH)CO_2Na$	11·7
$C_7H_5O_2^-$ (benzoate)	$C_6H_5CO_2K$	13·2
$C_4H_4O_4^{--}$ (succinate)	$C_2H_4(CO_2Na)_2$	14·0

* These solutions do not keep well and should be freshly prepared.

A, 4. COURSE OF INSTRUCTION

The following scheme of work is suggested for the guidance of beginners. It has been employed for some ten years at the Woolwich Polytechnic* with gratifying success. The standard ultimately attained is that required for the intermediate science degree of the University of London; the course is also suitable for the intermediate examinations of the other Universities, the higher school certificate examination, the preliminary scientific examination of the Pharmaceutical Society, the ordinary National Certificate in Chemistry, other examinations of similar standard, and for those requiring an elementary knowledge of qualitative analysis for any purpose. Modifications may, of course, be made by teachers according to the particular requirements of their students.

In the first place the student carries out the reactions of the cations of each group, as detailed below, and attempts to formulate equations for the most important reactions involved. His own results are then checked by reference to the text. The reactions at this early stage are composed largely of simple precipitations and the investigation of the solubilities of the precipitates in various reagents. After completing the reactions of a particular group, he should attempt to identify one or two cations in the group in the solution provided by the teacher or prepared by himself from the solids or test solutions available in the laboratory. This will familiarise the student at an early stage with the simple group separation table, and the previous study of the reactions should help him to understand most of the simple theory underlying the elementary group separation table.

Having completed the reactions of the cations, the student should proceed, on parallel lines, with the reactions of selected anions. (Those marked with two asterisks should be omitted.) When these have been carried out, he will be in a position to attempt the analysis of simple salts. With the aid of Table XXVI and the detailed model analysis given in Sect. **A, 5, (A)**, very little guidance should be required from the teacher. After 6–12 simple salts have been analysed, the student may then attempt the analysis of mixtures of two simple salts; the model analysis in Section **A, 5, (B)** will be found a useful guide.

REACTIONS OF THE CATIONS

Pb^{++}. Section **III, 2,** reactions *1, 2, 3, 4, 5, 6*; dry test.
Hg_2 Section **III, 3,** reactions *1, 2, 3, 4, 5, 6, 7*.
Ag^{+}. Section **III, 4,** reactions *1, 2, 3, 4, 5, 6*; blow-pipe test.

Identification of a metal in the solution supplied by the teacher by means of Table XVII (Section **III, 5**).

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Hg^{++}. Section **III, 6,** reactions *1, 2, 3, 4, 5, 6* ; dry test.
Bi^{+++}. Section **III, 7,** reactions *1, 2, 3, 4, 5, 6, 8* ; dry test.
Cu^{++}. Section **III, 8,** reactions *1, 2, 3, 4, 5, 6, 7, 8* ; dry test.
Cd^{++}. Section **III, 9,** reactions *1, 2, 3, 4, 5* ; dry test.

Identification of a metal or metals in the solution supplied by means of Table XVIII (Section **III, 10**).

As (ous). Section **III, 11,** reactions *1, 2, 3, 4, 5.*
As (ic). Section **III, 12,** reactions *1, 2, 3, 4* ; dry test.
Sb (ous). Section **III, 14,** reactions *1, 2, 3, 4, 5.*
Sb (ic). Section **III, 15,** reactions *1, 2, 3, 4* ; dry test.
Sn^{++}. Section **III, 16,** reactions *1, 2, 3, 4, 5.*
Sn^{++++}. Section **III, 17,** reactions *1, 2, 3, 4* ; dry tests (i) and (ii).

Identification of a metal or metals in the solution supplied by means of Table XIX (Section **III, 18**).

Fe^{++}. Section **III, 19,** reactions *1, 2, 3, 4, 5, 6, 7, 8.*
Fe^{+++}. Section **III, 20,** reactions *1, 2, 3, 4, 5, 6, 7, 8, 10* ; dry tests (i) and (ii).
Al^{+++}. Section **III, 21,** reactions *1, 2, 3, 4, 5, 6, 7* ; dry test.
Cr^{+++}. Section **III, 22,** reactions *1, 2, 3, 4, 5, 6* ; dry tests (i) and (ii).

Identification of a metal or metals in the solution supplied by means of Table XX (Section **III, 23**).

Co^{++}. Section **III, 24,** reactions *1, 2, 3, 4, 5, 6, 7* ; dry tests (i) and (ii).
Ni^{++}. Section **III, 25,** reactions *1, 2, 3, 4, 5, 6, 7, 8* ; dry tests (i) and (ii).
Mn^{++}. Section **III, 26,** reactions *1, 2, 3, 4, 5, 6* ; dry tests (i) and (ii).
Zn^{++}. Section **III, 27,** reactions *1, 2, 3, 4, 5, 6* ; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXI (Section **III, 28**).

Ba^{++}. Section **III, 29,** reactions *1, 2, 3, 4, 5, 6* ; dry test.
Sr^{++}. Section **III, 30,** reactions *1, 2, 3, 4, 5, 6* ; dry test.
Ca^{++}. Section **III, 31.** reactions *1, 2, 3, 4, 5, 6, 7* ; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXII (Section **III, 32**).

Mg^{++}. Section **III, 33,** reactions *1, 2, 3, 4, 5, 8* ; dry test.
K^{+}. Section **III, 34**, reactions *1, 2, 4* ; dry test.
Na^{+}. Section **III, 35,** reactions *1, 2* ; dry test.
NH_4^{+}. Section **III, 36,** reactions *1, 3, 5* ; dry test.

Identification of a metal or metals in the solution supplied by means of Table XXIII (Section **III, 38**).

REACTIONS OF THE ANIONS

CO_3^{--}. Section **IV, 2,** reactions *1, 2, 3.*
HCO_3^-. Section **IV, 3,** reactions (i), (ii), (iii), (iv), (v).
SO_3^{--}. Section **IV, 4,** reactions *1, 2, 3, 4, 5, 6, 7, 8, 9.*
$S_2O_3^{--}$. Section **IV, 5,** reactions *1, 2, 3, 4, 5, 6.*
S^{--}. Section **IV, 6,** reactions *1, 2, 3, 4, 5, 6.*
NO_2^-. Section **IV, 7,** reactions *1, 2, 3, 4, 5, 6, 7.*
***CN^-.** Section **IV, 8,** reactions *1, 2, 3, 4, 5, 6.*
Cl^-. Section **IV, 14,** reactions *1, 2, 3.*
Br^-. Section **IV, 15,** reactions *1, 2, 3, 4, 5.*
I^-. Section **IV, 16,** reactions *1, 2, 3, 4, 6, 7.*
F^-. Section **IV, 17,** reactions *1, 2, 3, 4.*
NO_3^-. Section **IV, 18,** reactions *1, 2, 3, 4, 7.*
SO_4^{--}. Section **IV, 24,** reactions *1, 2, 3.*
PO_4^{---}. Section **IV, 28,** reactions *1, 2, 3, 4, 5, 7.*
CrO_4^{--}. Section **IV, 33,** reactions *1, 2, 3, 4, 5, 6, 7.*

The student should now proceed with the analysis of several simple salts. Before attempting the identification of mixtures of simple salts, it is suggested that he should, subject to the approval of the teacher, carry out the reactions of the following anions.

BO_2^- (borate). Section **IV, 23,** reactions *1, 2, 3, 6.*
SiO_3^{--} (silicate). Section **IV, 26,** reactions *1, 2, 3, 5, 6.*
$C_2H_3O_2^-$ (acetate). Section **IV, 35,** reactions *1, 2, 3, 4, 5, 6, 7, 8.*
$C_2O_4^{--}$ (oxalate). Section **IV, 37,** reactions *1, 2, 3, 4, 5, 7.*
$C_4H_4O_6^{--}$ (tartrate). Section **IV, 38,** reactions *1, 2, 3, 4, 5, 6, 7.*

More advanced students should carry out the reactions of the anions that were omitted in the elementary course. They may then proceed, with the aid of Tables XXIV, XXV and XXVII–XXXVII, to the analysis of complex mixtures, insoluble substances and alloys. A model analysis is given in Section **A, 5, (C).** Concurrently with the laboratory work, a detailed study should be made of the whole book, particularly of Chapters I and VI and the detailed explanations of the group separation tables. A course of about nine lectures upon qualitative analysis is given at the Woolwich Polytechnic; these cover the experimental procedures to be adopted in the laboratory and a brief discussion of the underlying theoretical principles. The exact course to be pursued by an advanced student will depend upon the amount of time available, the ultimate object in mind, and the views (and prejudices) of his teachers. It is hoped that the contents of this volume will provide sufficient material to meet the requirements of most systems for the study of the subject.

* To be omitted unless carried out under the immediate supervision of the teacher.

A, 5. MODEL ANALYSES

The student should record the results of his experiments, preferably in ink, at the time they are made. An accurate record of all observations is thus obtained, and the possibility of such questions as " What exactly did I do ? " or " What did really happen ? " arising at a later date avoided. It is important that the student should cultivate the habit of employing the tabular form from the very outset ; he can then readily retrace his steps, if necessary, and the teacher (or examiner) can see at a glance all that he has done. Three typical analyses are given below : (*A*) a simple salt*, (*B*) a mixture of two simple salts, and (*C*) a complex mixture of six radicals. The first two are intended for the guidance of beginners, and the last for advanced students.

A. ANALYSIS OF THE SIMPLE SALT, NO. 7. Feb. 21st, 1937.

Description. White amorphous solid ; odourless ; non-magnetic.

Tested for ammonium. Heated solid with NaOH solution and held moist litmus paper or mercurous nitrate paper in the vapour. No change. Ammonium absent.

Tested for nitrate (**or nitrite**). Added a little Devarda's alloy (or aluminium powder) and warmed gently. No ammonia evolved. Nitrate and nitrite absent.

Preliminary Tests.

Experiment	*Observation*	*Inference*
(1) Heated solid in dry test-tube.	—	—
(2) Carried out flame test with a clean Pt wire.	Brick-red flame.	**Ca present.**
(3) Heated on charcoal with a blow-pipe.	—	—
(4) Borax bead test.	—	—
(5) Treated solid with dilute HCl.	Vigorous effervescence, colourless gas evolved, renders lime water turbid.	**Carbonate present.**
(6) Treated solid with 1 c.c. of conc. H_2SO_4.	Results similar to (5) but more vigorous.	

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* For elementary students, the term **simple salt** is employed in the sense of a substance containing one metallic and one acidic radical.

How solution made. Substance insoluble in hot and cold water. Soluble in dilute HCl accompanied by effervescence.

Separation into Groups.

<table>
<tr><td colspan="6">Diluted and cooled solution.</td></tr>
<tr><td rowspan="5">No ppt. Group I absent.</td><td colspan="5">Passed H_2S for several minutes, boiled and passed H_2S again.</td></tr>
<tr><td rowspan="4">No ppt. Group II absent.</td><td colspan="4">Boiled off H_2S, added 2 c.c. of conc. HNO_3, boiled, and then added 1–2 grams of NH_4Cl and a slight excess of NH_4OH solution.</td></tr>
<tr><td rowspan="3">No ppt. Group IIIA absent.</td><td colspan="3">Added ammonium sulphide solution to a portion of the solution.</td></tr>
<tr><td rowspan="2">No ppt. Group IIIB absent.</td><td colspan="2">Concentrated the remainder of the solution to about one third of its bulk, added excess of $(NH_4)_2CO_3$ solution and allowed to stand 5 minutes. Filtered.</td></tr>
<tr><td>Residue. White. Group IV present.</td><td>Filtrate.* Evaporated to small bulk. Divided into two unequal parts.
(i) Added Na_2HPO_4 and NH_4OH solution: rubbed sides of test-tube with glass rod.
No ppt. Mg absent.
(ii) Second portion evaporated to dryness until all fuming ceased. No residue.
Na and K absent.</td></tr>
</table>

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* After one metal has been found, it is really unnecessary to work through the remainder of the Table, but it is given here for the sake of completeness.

Analysis of Group IV ppt.

<table>
<tr><td colspan="3">Dissolved ppt. in dilute acetic acid. Added K_2CrO_4 solution to a small portion.</td></tr>
<tr><td rowspan="2">No ppt.
Ba absent.</td><td colspan="2">To half of the remainder of the solution added $CaSO_4$ solution, boiled and allowed to stand for 5 minutes.</td></tr>
<tr><td>No ppt.
Sr absent.</td><td>Added NH_4OH and $(NH_4)_2C_2O_4$ solutions to the remainder of the solution.
White ppt., insoluble in acetic acid.
Ca present.
Ppt. was filtered off and flame test applied. Brick-red flame.</td></tr>
</table>

Tests for Acid Radicals.*

Tabulate in form :

Experiment	*Observation*	*Inference*

Conclusion. The given salt No. 7 is calcium carbonate.

Note. If the anion is not detected by the action of dilute or conc. H_2SO_4 in the preliminary tests, it is necessary to prepare a ***neutral** solution,* free from heavy metals, as follows. Boil 2 grams of the solid with 15 c.c. of a saturated solution of sodium carbonate for

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* In this particular example of a simple salt no further tests are necessary as carbonate has been found and confirmed in the preliminary tests. The student should cultivate the habit of using this immediately after the cations have been detected and confirmed.

5 minutes (conical flask with funnel in mouth), filter, reject the ppt. (if any), and render filtrate faintly acid with dilute HNO_3. Boil to expel CO_2, add NH_4OH solution until just alkaline, boil until neutral, *i.e.*, until NH_3 cannot be detected in the vapour with mercurous nitrate paper.

Test neutral solution with (*a*) $BaCl_2$ solution and dilute HCl (for sulphate, etc.), (*b*) with $AgNO_3$ solution (for chloride, bromide, iodide, phosphate, arsenite, arsenate, chromate, etc.). Nitrate should be tested for by the brown ring test either with the original solution (if soluble in water) or upon an aqueous extract of the original substance, since all nitrates are soluble in water.

B. ANALYSIS OF MIXTURE, NO. I 77. Feb. 17th, 1937.

Description. Bluish-green crystalline solid; odourless; non-magnetic.

Tested for ammonium. Heated solid with NaOH solution and held moist mercurous nitrate paper in vapour. No colouration. Ammonium absent.

Tested for nitrate (nor nitrite). Added a little Devarda's alloy (or aluminium powder) and warmed gently. No ammonia evolved. Nitrate and nitrite absent.

Preliminary Tests.

Experiment	*Observation*	*Inference*
(1) Heated substance in dry tube.	Water vapour evolved; mass assumes a yellow colour.	Water of crystallisation.
(2) Carried out flame test with a clean Pt wire.	Green flame.	Copper (?), Barium (?).
(3) Heated on charcoal with a blow-pipe.	Inconclusive.	
(4) Borax bead test.	Inconclusive.	
(5) Treated solid with dilute H_2SO_4 and warmed.	No positive result.	
(6) Treated solid with conc. H_2SO_4.	Gas evolved on gentle warming; white fumes on blowing across mouth of tube.	HCl from chloride.

How solution made. Mixture was soluble in water.

Separation into Groups.

<table>
<tr><td colspan="6">Added dilute HCl to aqueous solution and cooled.</td></tr>
<tr><td rowspan="5">No ppt.
Group I absent.</td><td colspan="5">Passed H_2S; diluted somewhat, boiled and passed H_2S. Filtered and washed.</td></tr>
<tr><td rowspan="4">Residue. Black.
Group II present.</td><td colspan="4">Filtrate. Boiled off H_2S, added 2 c.c. of conc. HNO_3 and boiled. Tested 1 c.c. of solution with ammonium molybdate solution and HNO_3; no yellow ppt. Phosphate absent. Added 2 grams of NH_4Cl, boiled and then slight excess of NH_4OH solution.</td></tr>
<tr><td rowspan="3">No ppt.
Group IIIA absent.</td><td colspan="3">Added ammonium sulphide solution and filtered.</td></tr>
<tr><td rowspan="2">Residue. Black.
Group IIIB present.</td><td colspan="2">Filtrate. Dark-coloured; acidified with dilute acetic acid, boiled and filtered off slight ppt. (*A*).
Filtrate was concentrated to one-third bulk, NH_4OH solution and excess of $(NH_4)_2CO_3$ solution added, and allowed to stand for 5 minutes.</td></tr>
<tr><td>No ppt.
Group IV absent.</td><td>Evaporated to small bulk. Divided into two parts. Tested one portion for Mg by "magneson" test.
Mg absent.
Other portion evaporated to dryness until fuming ceased. No residue.
Group V absent.</td></tr>
</table>

Analysis of Group II ppt.

<table>
<tr><td colspan="2">The washed ppt. was warmed with 10 c.c. of yellow ammonium sulphide solution for 3–4 minutes, and filtered.</td></tr>
<tr><td>Residue. Black.
Group IIA present.</td><td>Filtrate. Acidified with HCl and warmed gently. Fine white ppt. of sulphur.
Group IIB absent.</td></tr>
</table>

Analysis of Group IIA ppt.

<table>
<tr><td colspan="3">Warmed with dilute HNO_3.</td></tr>
<tr><td rowspan="2">Ppt. dissolved completely.
Hg absent.</td><td colspan="2">Tested portion of solution for Pb by adding dilute H_2SO_4 and alcohol. No ppt. Pb absent.
Added excess of NH_4OH solution to the remainder of the solution.</td></tr>
<tr><td>No ppt.
Bi absent.</td><td>Blue solution produced. Cu present.
Confirmed Cu by adding $K_4[Fe(CN)_6]$ solution and acetic acid ; brown ppt.
Added KCN solution drop by drop until solution decolourised and passed H_2S. No ppt. Cd absent.</td></tr>
</table>

Analysis of Group IIIB ppt.

<table>
<tr><td colspan="3">Washed ppt. Treated in beaker with very dilute HCl (1 : 10) and filtered after 2–3 minutes.</td></tr>
<tr><td rowspan="2">Residue. Black.
Co and/or Ni present.
Tested with borax bead ; reddish-brown in oxidising flame and grey in reducing flame. This indicates presence of Ni and absence of Co. Dissolved residue in aqua regia and evaporated just to dryness. Dissolved residue in a little water, added NH_4Cl and NH_4OH solutions followed by excess of dimethyl glyoxime reagent. Red ppt. Ni present.</td><td colspan="2">Filtrate. Boiled off H_2S and added excess of NaOH solution.</td></tr>
<tr><td>No ppt.
Mn absent.</td><td>Passed H_2S
No ppt.
Zn absent.</td></tr>
</table>

Tests for Acid Radicals.

Prepared a **neutral solution**, free from heavy metals, by boiling 2 grams of the mixture with excess of saturated Na_2CO_3 solution for 10 minutes ; filtered, acidified filtrate with dilute HNO_3, boiled to expel CO_2, added a slight excess of NH_4OH solution, and boiled off the excess of ammonia.

Experiment	*Observation*	*Inference*
Added conc. H_2SO_4 to solid, then a little pptd. MnO_2, and warmed.	Greenish gas evolved, choking odour, reddens and then bleaches litmus paper, and also turns potassium iodide-starch paper blue.	**Cl_2 from chloride.**
Added $AgNO_3$ solution to neutral solution.	Curdy white ppt. readily soluble in dilute NH_4OH solution, repptd. by HNO_3.	**Chloride present.**
Added $BaCl_2$ solution and dilute HCl to neutral solution.	White ppt.	**Sulphate present.**

Confirmed sulphate by fusing ppt. with Na_2CO_3 upon charcoal, extracting residue with a little water, and filtering into freshly prepared sodium nitroprusside solution. Purple colouration.

Conclusion. The mixture *I 77* contains Cu^{++}, Ni^{++}, Cl^-, SO_4^{--}, and water of crystallisation.

C. ANALYSIS OF MIXTURE, NO. S 7. Feb. 7th, 1937.

Description. White amorphous powder; slightly deliquescent; non-magnetic.

Tested for ammonium: by heating with NaOH solution and holding mercurous nitrate paper in the vapour. Paper became black. **Ammonium present.**

Tested for nitrate (or **nitrite**). Continued heating with NaOH solution until ammonia was no longer evolved. Cooled, added a little Devarda's alloy, and warmed gently. Ammonia was evolved as indicated by the mercurous nitrate paper and litmus paper tests. **Nitrate or nitrite present.**

Preliminary Tests.

Experiment	*Observation*	*Inference*
(1) Heated substance in dry tube.	(*a*) Small white sublimate, odour of NH_3.	**Ammonium salts.**
	(*b*) Slight charring.	Organic acids (?).
(2) Carried out flame test with clean Pt wire.	Crimson flame.	Strontium.
(3) Heated on charcoal with a blow-pipe.	White infusible residue.	Possibly Al, Mg, phosphates or silicates.
Added 2 drops of $Co(NO_3)_2$ solution and heated again.	Pale-blue residue.	
(4) Borax bead test.	Inconclusive.	
(5) Treated solid with dilute H_2SO_4 and warmed.	No positive result.	
(6) Treated solid with conc. H_2SO_4 and warmed.	Pungent acid fumes evolved; slow charring.	Organic acid (?).
Added Cu turnings and warmed again.	Brown fumes evolved.	**Nitrate.**

How solution made. The mixture was partially soluble in boiling water, but completely soluble in dilute HCl.

Separation into Groups.

<table>
<tr><td colspan="6">The HCl solution was thoroughly cooled.</td></tr>
<tr><td rowspan="7">No ppt. Group I absent.</td><td colspan="5">Adjusted solution to correct hydrogen ion concentration (*p*H) with brilliant cresyl blue. Warmed solution and passed H_2S.</td></tr>
<tr><td rowspan="6">No ppt Group II absent.</td><td colspan="4">Boiled off H_2S, added 3–4 c.c. of conc. HNO_3 and evaporated just to dryness. Repeated treatment with conc. HNO_3 until all the black particles of *C* had disappeared.
Added 15 c.c. of dilute HCl to residue; it dissolved completely. Silicate absent.
Tested 1 c.c. of solution with ammonium molybdate solution and HNO_3; yellow ppt. on gentle warming. **Phosphate present.** Tested a further 1 c.c. for Fe with $K_4[Fe(CN)_6]$ solution—Fe absent.
Added 1–2 grams of solid NH_4Cl, boiled, and then a slight excess of NH_4OH solution, and filtered.</td></tr>
<tr><td colspan="2">**Residue** (*A*). White. Groups IIIA–IV or Mg may be present.</td><td colspan="2">**Filtrate** (*B*). Did not give phosphate test with ammon. molybdate.</td></tr>
<tr><td colspan="4">Dissolved ppt. *A* in the minimum volume of dilute HCl, added dilute NH_4OH solution until a faint permanent ppt. was obtained. Added 2–3 c.c. of dilute acetic acid and 3–4 c.c. of saturated ammonium acetate solution; solution remained colourless. Added $FeCl_3$ solution drop by drop until solution was just red, diluted to 150 c.c., boiled for 2–3 minutes and filtered hot.</td></tr>
<tr><td rowspan="3">**Residue** (*C*). Reddish-brown. May contain Cr and Al.</td><td colspan="3">**Filtrate.** Concentrated to 15 c.c., and combined with filtrate *B*. Added 0·5 gram of NH_4Cl and a slight excess of NH_4OH solution; no ppt. was obtained. Saturated hot solution with H_2S.</td></tr>
<tr><td rowspan="2">No ppt. Group IIIB absent.</td><td colspan="2">Concentrated to 20 c.c., added NH_4OH solution and then excess of $(NH_4)_2CO_3$ solution. Warmed gently and filtered.</td></tr>
<tr><td>**Residue.** White. **Group IV present.**</td><td>**Filtrate.** Divided into two unequal parts. Evaporated smaller portion to dryness until all ammonium salts volatilised.
White residue. **Group V present.**</td></tr>
</table>

Analysis of Residue (C).

Added 15 c.c. of water, and then 1·5 grams of Na_2O_2 in small portions. Boiled for 5 minutes, diluted and filtered.	
Residue. $FePO_4$ and $Fe(OH)_3$. Rejected.	**Filtrate.** Colourless; Cr absent. Added 2 grams of solid NH_4Cl, boiled until NH_3 ceased to be evolved. No ppt. Al absent.

Analysis of Group IV ppt.

Dissolved ppt. in dilute acetic acid. Tested 2 c.c. for Ba by heating to boiling and adding K_2CrO_4 solution drop-wise.		
No ppt. Ba absent.	Divided remainder of the solution into two equal parts.	
	Part I. Added *ca.* 3 grams of NH_4Cl and 5 c.c. of conc. $K_4[Fe(CN)_6]$ solution Allowed to stand. No ppt. Ca absent.	*Part II*, Added NH_4OH solution and excess of $(NH_4)_2CO_3$ solution. White ppt. **Sr present.** Filtered off ppt. dissolved in conc. HCl, evaporated to dryness, and applied flame test; crimson flame.

Analysis of Group V residue.

Added 1–2 c.c. of $(NH_4)_2SO_4$ solution and 1–2 c.c. of $(NH_4)_2C_2O_4$ solution to the main filtrate from Group IV; heated, allowed to stand, and filtered from a minute quantity of ppt. Divided filtrate into two parts.	
Smaller portion	*Larger portion*
Evaporated to dryness, dissolved residue in a little dilute HCl, added a few drops of "magneson" reagent, followed by excess of 1% NaOH solution. Flocculent blue ppt. **Mg present.**	Evaporated to dryness until all ammonium salts volatilised. Applied flame test to residue. Na and K absent.

Tests for Acid Radicals.

Prepared a **neutral solution**, free from heavy metals, by boiling 2 grams of the mixture with excess of saturated Na_2CO_3 solution (a little solid Na_2CO_3 was present) under reflux for 15 minutes, and filtered. The filtrate was acidified with dilute HNO_3, boiled to expel CO_2, a slight excess of NH_4OH solution added and the excess of ammonia boiled off.

Experiment	*Observation*	*Inference*
Added conc. $FeSO_4$ solution to aqueous extract of original mixture, then poured conc. H_2SO_4 carefully down side of test-tube.	Brown ring formed.	**Nitrate present.**
Added $BaCl_2$ and HCl to neutral solution.	No ppt.	Sulphate and silicofluoride absent.

Identification of Organic Acids.

<table>
<tr><td colspan="4">Added $CaCl_2$ solution to cold neutral solution, rubbed sides of test-tube with glass rod and allowed to stand for 10 minutes. Filtered.</td></tr>
<tr><td colspan="2">Residue. White.
Treated small portion with dilute acetic acid.</td><td colspan="2">Filtrate. Added more $CaCl_2$ solution, boiled under reflux for 5 minutes, and filtered.</td></tr>
<tr><td>Dissolved completely. Oxalate absent.</td><td>Dissolved portion in HNO_3 and tested with ammon. molybdate solution. Yellow ppt.
Phosphate present.
Tested neutral solution with Fenton's reagent. No blue colouration.
Tartrate absent.</td><td>Residue. White.
Citrate present.
Confirmed citrate by dissolving ppt. in dilute HCl, preparing neutral solution, and adding $CdCl_2$ solution. White gelatinous ppt.
Also by Denigès' test.</td><td>Filtrate.
Added $FeCl_3$ solution. No colouration or ppt.
Acetate, formate, benzoate, succinate and salicylate absent.</td></tr>
</table>

Conclusion. The mixture *S 7* contains Sr^{++}, Mg^{++}, NH_4^+, NO_3^- PO_4^{---}, $C_6H_5O_7^{---}$ (citrate).

A, 6. SOLUBILITIES OF SALTS AND BASES IN WATER AT 18°C.*

	K	*Na*	*Li*	*Mg*	*Ba*	*Sr*	*Ca*	*Zn*	*Pb*	*Ag*
Cl	32·95	35·86	77·79	55·81	37·24	51·09	73·19	203·9	1·49	1·4 × 10^{-4}
Br	65·86	88·76	168·7	103·1	103·6	96·52	143·3	478·2	0·97	1 × 10^{-3}
I	137·5	177·9	161·5	148·2	201·4	169·2	200·0	419·0	0·08	3·0 × 10^{-7}
F	92·56	4·44	0·27	0·0076	0·16	0·012	0·0016	0·005	0·06	195·4
NO_3	30·34	83·97	71·43	74·31	8·74	66·27	121·8	117·8	51·66	213·4
ClO_3	6·6	97·16	313·4	126·4	35·42	174·9	179·3	183·9	150·6	12·25
BrO_3	6·38	36·67	152·5	42·86	0·8	30·0	85·17	58·43	1·3	0·59
IO_3	7·62	8·33	80·43	6·87	0·05	0·25	0·25	0·83	0·002	0·004
SO_4	11·11	16·83	35·64	35·43	2·3 × 10^{-4}	0·011	0·20	53·12	0·0041	0·55
CrO_4	63·1	61·21	111·6	73·0	3·8 × 10^{-4}	0·12	0·4	—	2 × 10^{-5}	0·0025
C_2O_4	30·27	3·34	7·22	0·03	0·0086	0·0046	5·6 × 10^{-4}	7·9 × 10^{-4}	0·0001	0·0035
CO_3	108·0	19·39	1·3	0·1	0·0023	0·0011	0·0013	—	0·0001	0·003
OH	142·9	116·4	12·04	0·001	3·7	0·77	0·17	0·0005	0·01	0·002 (?)

* The solubilities are expressed in grams of anhydrous salt dissolved by 100 c.c. of water.

A, 7.—Selected Literature References to Micro-qualitative Analysis (Separations)

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I. *Mitteilung.*
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A, 8. LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 4	9 8	13 12	17 16	21 20	26 24	30 28	34 32	38 37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 4	8 7	12 11	15 15	19 19	23 22	27 26	31 30	35 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 3	7 7	11 10	14 14	18 17	21 20	25 24	28 27	32 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 3	7 7	10 10	13 12	16 16	20 19	23 22	26 25	30 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 3	6 6	9 9	12 12	15 15	18 17	21 20	24 23	28 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 3	6 5	9 8	11 11	14 14	17 16	20 19	23 22	26 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 3	5 5	8 8	11 10	14 13	16 15	19 18	22 21	24 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 2	5 5	8 7	10 10	13 12	15 15	18 17	20 19	23 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 2	5 5	7 7	9 9	12 11	14 14	16 16	19 18	21 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 2	4 4	7 6	9 8	11 11	13 13	16 15	18 17	20 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	66·5	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7529	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	3	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

A, 8. ANTI-LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1137	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2814	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTI-LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	9
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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